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The Debye temperatures of copper-rich, Cu-Au alloys

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by

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I. INTRODUCTION

Much have I traveled in the realms of gold,
And many goodly states and kingdoms seen.

Keats - On First Looking into Chapman's Homer

A. Statement of Thesis

Many aspects of the Cu-Au alloy system have come under investigation within the last fifty years, after Johansson and Linde established the continuity of the solid solution and the existence of ordered compositions (1, 2). With one valence electron per atom for each specie, the electronic structure of the pure species and their alloys may be presumed to be uncomplicated, although the rather large size disparity must introduce a factor of strain energy to the solid solution. Yet, explanations of the behavior of many properties remain enigmas, implying that the electronic structure and vibrational spectra do vary with composition, in short, that the rigid band theory does not describe even dilute Cu-Au alloys.

To support this hypothesis, two basic characteristics of copper-rich, Cu-Au alloys were investigated, electrical resistivity and elastic moduli. The first has been measured previously, however, the extent of the heat treatments coupled with the precision and completeness of this investigation constitutes a significant improvement. Other than determination of the

elastic moduli of Cu_3Au (3), values for no other composition have been measured.

B. Historical Retrieve of Cu-Au Investigations

More specifically, lattice parameters of alloys in the system Cu-Cu_3Au have been measured by several investigators (3-8). An outline of their results is given in Table 1. No unified work has been carried out for very slowly-cooled alloys, i.e., those which approach equilibrium at room temperature, and it is difficult to infer the nuances in slope or curvature which mark changes in the atomic distributions in an alloy system. This latter work has now been done in a previous investigation by Dr. F. X. Kayser and myself (W. H. Cullen and F. X. Kayser, unpublished research, 1971).

Similarly, a tabular summary of the published electrical resistivity data is presented in Table 2 (8-12). Again, no measurements of the residual resistivity for slowly-cooled dilute alloys are available, nor has an adequate analysis of the thermal component of the resistivity been carried through for a range of alloys.

Cast against this background, more complete and precise examinations of Cu-Au alloys do not seem redundant, but indeed, may betray the best-kept secrets which have sustained the interest of physicists and metallurgists for over half a century.

Conceptually, then, I am dealing with two isoelectronic species which form a continuous series of solid solutions in spite of their large size disparity. I wish to examine the

Table 1. An outline of previous lattice parameter measurements on copper-rich, Cu-Au alloys

Authors	Composition (at. % Au)	Lattice Parameter (Å)	Heat treatment
Flinn, McManus, Rayne (3)	24.94	3.7490/25°C	Water-quenched from 775°C
	Same	3.7426/25°C	370°C/70 hrs., quenched, 230°C/170 hrs.
Ageew, Shoyket (4)	20.18	3.668/[a]	500°C/24 hrs., cooled from 500°C to ambient over 10 days.
	22.68	3.684/[a]	Same
	24.90	3.746/[a]	Same
Nix, MacNair (5)	22.1	3.737/a	600°C/10 hrs., oil-quenched
	24.8	3.754/a	Same
	22.1	3.725/a	Just below transition temperature for 70 hrs., cooled at 5°C/hr. to 250°C
	24.8	3.739/a	Same
Owen, Sim (6)	25.0	3.7529/18°C	Disordered
	Same	3.7478/18°C	350°C, quenched
Betteridge (7)	24.09	3.7456/20°C	(1) 370°C/114 hrs., 350°C/96 hrs., quenched
	Same	3.7448/20°C	(2) As (1) + 300°C/96 hrs.
	Same	3.7444/20°C	(3) As (2) + 250°C/96 hrs.
	Same	3.7442/20°C	(4) As (3) + 200°C/96 hrs.
Hirabayashi, Muto (8)	5.06	3.6448/a	450°C, quenched
	25.07	3.7534/a	Same

[a]Temperature not given, ambient may be presumed

Table 2. An outline of previous resistivity measurements on slowly-cooled, copper-rich, Cu-Au alloys

Authors	Composition (at. % Au)	Total resistivity at temperature (micro-ohm-cm at °K)					
Linde (9)	0.00			1.712	@ 291°K		
	0.50			1.954	"		
	0.99			2.200	"		
	1.99			2.811	"		
	2.39			3.072	"		
	3.00			3.278	"		
Grube et al. (10)	0.00			1.68	@ 293°K		
	10.00			6.50	"		
	15.01			8.43	"		
	17.01			9.65	"		
	18.93			9.35	"		
	20.01			9.03	"		
	20.78			6.86	"		
	22.93			5.70	"		
	24.08			4.38	"		
	24.97			4.14	"		
Pospisil (11)	10.00	6.22	@ 273°K	4.81	@ 77.4°K	4.51	@ 20.4°K
	15.01	8.27	"	6.82	"	6.48	"
	17.51	9.39	"	7.89	"	7.55	"
	18.93	9.78	"	----	"	----	"
	20.01	9.77	"	7.78	"	7.22	"
	21.07	7.35	"	5.21	"	4.66	"
	21.55	9.23	"	7.30	"	6.79	"
	22.93	6.00	"	3.68	"	3.09	"
	24.08	4.64	"	2.27	"	1.66	"
	24.98	4.86	"	2.46	"	1.85	"
	24.98	4.34	"	1.97	"	1.37	"

Table 2. (Continued)

Authors	Composition (at. % Au)	Total resistivity at temperature (micro-ohm-cm at ^{o}K)
Hirabayashi, Muto (8)	5.06	5.10 @ 273^{o}K
Passaglia, Love (12)	25.0	0.272 @ 4.2^{o}K

variation of the Debye temperatures (θ_D), which gives some insight into the variation of the vibrational spectra with composition and temperature. Methodologically, I have two basic thrusts, both on carefully prepared, very slowly-cooled alloys. The first is to examine the thermal and compositional dependence of the electrical resistivity and use the Bloch-Gruneisen formula (13, 14) to evaluate a characteristic θ_R for each specimen. The second is to measure the ultrasonic velocities in oriented single crystals, to calculate and evaluate the elastic moduli, and to use the method of Jules de Launay (15) to evaluate a characteristic θ_{el} for each specimen. While these two cannot be compared on an absolute basis, I will be able to examine the effect of the alloying and temperature on the phonon spectra, through the effect of the phonon spectra on the electrical and elastic properties of these alloys.

II. APPLICATION OF DEBYE THEORY

...m.a.W., die spezifische Wärme für alle (einatomigen) Körper ist eine universalle Funktion des Verhältnisse T/θ.

Bei genugend niedrigen Temperaturen ist die spezifische Wärme aller Körper der dritten Potenz der absoluten Tempertur proportional.

...in other words, the specific heat of all (monatomic) substances is a universal function of the ratio T/θ.

At sufficiently low temperatures, the specific heat of all substances is proportional to the third power of the absolute temperature.

P. Debye - On the Theory of Specific Heat

A. Experimental Methods of Determining Debye Temperatures

Peter Debye (16) originally formulated his theory of the distribution of frequencies in an isotropic, elastic continuum. This parabolic distribution holds up to a cut-off frequency, ν_D, which is incorporated in the definition of the Debye temperature:

$$\theta_D = \frac{h}{k}\nu_D \qquad (1)$$

Excellent reviews of the origins of this theory, documenting its enormous initial success in the fields of specific heat and elasticity, have been published (17, 18) and any further elaboration here is redundant.

While we are well aware that the actual distribution of frequencies in a solid is not parabolic in nature, and that solids are not usually isotropic in the elastic sense, the

characterization of metals, alloys and other substances continues, largely because no better, simple, common ground exists for the comparison of the effective vibrational spectra of two media.

Under this overall proviso, a Debye temperature of some meaning will characterize the results of several different types of measurements: specific heat (Θ_D), elastic constants (Θ_{el}), electrical resistivity (Θ_R), X-ray diffraction (Θ_M) and others. In each of these phenomena, the nature of the frequency spectrum plays a different role, and naturally, a different Debye theta will be derived. This leads to the statement which forms the milieu for this dissertation: Choosing a Debye temperature amounts to choosing the phenomenological parameter defining the limits of the parabolic representation which best describes the vibrational spectrum under the conditions of averaging of the particular method.

Figure 1 is a graphical compendium of Debye temperatures of Cu-Au alloys calculated by several experimental methods (3, 8, 12, 19-22). While not an omnibus survey, I have tried to indicate three salient features: 1. the close agreement between the $0^{\circ}K$ values calculated from specific heat measurements (calorimetry) and elastic constants. 2. The disparity in absolute values expected and found between different types of measurements, particularly noticeable for the Cu_3Au composition, but also, 3. the behavioral consistency between the values calculated in the same way from similarly prepared

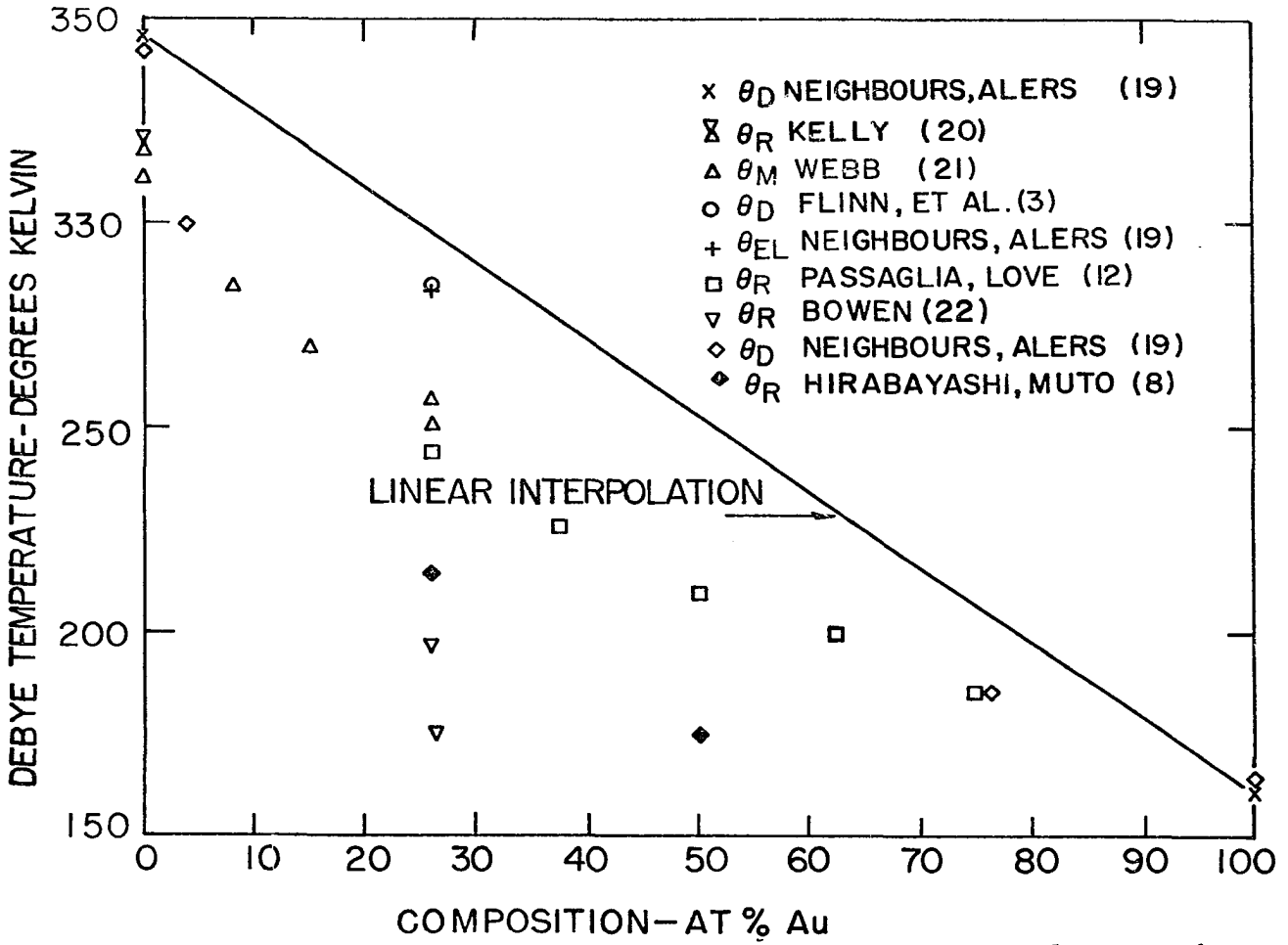


Figure 1. The Debye temperatures of Cu-Au alloys as calculated from various types of investigations as a function of composition

alloys of different composition. In the latter sense, note the resistivity data of Passaglia and Love, and the X-ray data of Webb. In the ensuing analysis of Debye temperatures, this dissertation will bear on each of these three points.

B. Derivation of θ_R

E. Gruneisen suggested in 1933 (14) that an equation created by F. Bloch in 1928 (13) and intended for use only at low temperatures might be applicable at intermediate temperatures also. This equation can be written in the form:

$$\rho(T) = \frac{CT}{M\theta_R^2} (T/\theta_R)^4 \int_0^{\theta_R/T} \frac{z^5 dz}{(e^z - 1)(1 - e^{-z})} \qquad (2)$$

$$= \frac{C}{4M} (T/\theta_R^2)\, G(\theta_R/T) \qquad (3)$$

in which C is a constant, M is an atomic mass, and $G(\theta_R/T)$ has come to be known as the Gruneisen function and is real and finite for all non-negative values of θ_R/T.

Although the Bloch-Gruneisen formulation of the theoretical electrical resistance of metals rests on some very limiting assumptions, the model has been bastardized and its use extended to metals and alloys in all temperature ranges. Blackman (23) has campaigned at length to clarify earlier misconceptions that θ_R--the Debye temperature calculated from the Bloch-Gruneisen formulation--bears any connection to θ_D or θ_{el}, the reason being that only longitudinal, rather than transverse vibrations play a role in the electrical resistance

of a metal. Nevertheless, the empirical fact remains that there are often remarkable correlations between θ_R and θ_D which have led to continued use of the Bloch-Gruneisen format.

I wish to make it clear at the outset that there is very little theoretical basis for the use of the Bloch-Gruneisen form of the electrical resistance for alloys, and in the temperature range ($140^{\circ}K$-$260^{\circ}K$) of interest. The results which appear are constructed only for the purpose of intra-comparison and should not be considered in an absolute sense.

C. Derivation of θ_{el}

On the other hand, the calculation of Debye temperatures from the low-temperature elastic moduli does rest on firm theoretical and empirical ground. The actual calculation rests on the numerical integration of the three unique modes of sound waves in a crystal over an element of solid angle. Perhaps the most commonly used means to this end is the utilization of tables prepared by Jules de Launay. These tables yield a function which, when combined with other crystal parameters, yields the Debye theta. The details of the method have been published by de Launay (15) and reviewed by Alers (24).

Briefly, the mathematical relations between the thermal vibrations of an elastic continuum, the Debye temperature and the ultrasonic velocities are as follows (24, 25).

An elastic continuum will support thermal, acoustic waves of frequency ν and wavelength λ according to the usual form

$$\nu = c_s/\lambda_s \tag{4}$$

where c_s is the velocity of the wave. In all real media, three types of waves (one compressional (longitudinal) and two independent transverse (shear)) can be propagated and the velocity is given by an average of these

$$\frac{1}{c_s^3} = \int_{\Omega} \left[\frac{1}{c_1^3} + \frac{1}{c_2^3} + \frac{1}{c_3^3} \right] \frac{d\Omega}{4\pi}, \tag{5}$$

where $d\Omega$ is an element of solid angle in k-space. The three dimensional wave equation for an elastic continuum is

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = \frac{1}{c_s^2}\frac{\partial^2 u}{\partial t^2} \tag{6}$$

For a general solution,

$$u(x,y,z,t) =$$

$$A \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) \cos\,(2\pi\nu t) \tag{7}$$

the possible frequencies are specified by

$$\nu = \frac{(n_x^2 + n_y^2 + n_z^2)^{1/2}\, c_s}{2L} = \frac{c_s R}{2L} \tag{8}$$

where $R = (n_x^2 + n_y^2 + n_z^2)^{1/2}$ is an **n-space radius vector norm**.

The frequency density function, or the number of possible modes between ν and $\nu + d\nu$ is the number of R-vectors terminating in a spherical shell in n-space.

$$N(\nu)d\nu = \frac{1}{8} 4\pi R^2 dR = \frac{\pi}{2} \frac{2L\nu}{c_s}^2 \frac{2L\nu}{c_s} d\nu \tag{9}$$

By using equation 5 and letting $V = L^3$ = volume of solid, then

$$N(\upsilon)d\upsilon = 4\pi V\upsilon^3 d\upsilon \int_{\Omega}\left[\frac{1}{c_1^3} + \frac{1}{c_2^3} + \frac{1}{c_3^3}\right]\frac{d\Omega}{4\pi} \qquad (10)$$

The fact that the crystal consists of N atoms is introduced by limiting the total number of vibrational modes to 3N, thus establishing a cut-off frequency which defines θ_D at low temperatures.

$$3N = \int_0^{\upsilon_D} N(\upsilon)d\upsilon = \frac{4}{3}\pi V\upsilon_D^3 \int_{\Omega}\left[\frac{1}{c_1^3} + \frac{1}{c_2^3} + \frac{1}{c_3^3}\right]\frac{d\Omega}{4\pi} \qquad (11)$$

or

$$\frac{1}{\theta_D^3} = \left(\frac{k}{h}\right)^3 \frac{1}{\upsilon_D^3} = \frac{4\pi V}{3N} \int_{\Omega}\left[\frac{1}{c_1^3} + \frac{1}{c_2^3} + \frac{1}{c_3^3}\right]\frac{d\Omega}{4\pi} \qquad (12)$$

It is the integration of the sound velocities over the k-space volume which presents the analytic difficulty. Hence the popularity of de Launay's tables, which, in the long-wavelength, low-temperature limit, give the same result as direct numerical integration of equation 12. For higher temperatures, there is no basis for direct comparison of de Launay's θ_{el} and θ_D. At higher temperatures, the velocity of a wave is dependent on the wavelength, i.e., there is a dispersion relation for the shorter wavelength phonons, and the integration of equation 11 is no longer valid.

III. ANALYSIS OF ELECTRICAL RESISTIVITY

One must be careful not to overinterpret the fit even of a one-parameter theory.

J. M. Ziman - Interactions between Electrons and Lattice Vibrations

The temperature variation of ρ_I is enshrined in the parameter θ_R...which turns out to be very close to the ordinary Debye temperature θ_D derived from the lattice specific heat...

J. M. Ziman - The Ordinary Transport Properties of the Noble Metals

---

A. Experimental Procedure

Careful examination of the residual resistivity and the thermal dependence of the resistivity can yield much information about the properties of the metallic lattice. I carried out an analysis of these topics to show that the effect of the changing vibrational structure is reflected in the behavior of the electrical resistance of copper-gold alloys.

Resistivity specimens were fabricated by swaging arc-melted ingots into rods ~0.100 in. in diameter and ~7 in. long, centerless-grinding these to rods 0.0600 in. $\pm$ .00025 in. in diameter, and carefully heat treating to bring them as close to equilibrium as possible. All heat treating was done in type 310 steel retorts, under a dynamically ion-pumped vacuum which had been fore-pumped by a low-temperature chemical adsorption canister. This process is indicative of the care

taken to prevent contamination in all phases of experimental preparation of these and other samples. Furnace temperatures were slowly increased to provide time for outgassing of the retort and its contents. The annealing scheme for these and other specimens is as follows:

1. Heat to 800°C for five or more days, depending on homogenization needs. Vacuum will be of the order of 10^{-6} torr.
2. Cool to 450°C and hold until vacuum is less than 10^{-7} torr.
3. Slowly and uniformly cool from 450°C to 150°C over a period of 90-100 days. Vacuum will be of the order of 10^{-8} torr upon completion of this scheme.

Metallography of these samples showed that the grains had a high density of annealing twins, and that the grain size was from 10 to 15 microns, and independent of composition. Since grain sizes of about 10 microns or larger cause spotty X-ray powder patterns, these specimens lie at the upper limit for precision lattice parameter measurements. Experience showed that peak position measurements within standard deviations of 0.005 degrees were possible and this accuracy provides the necessary precision in the calculation of lattice parameters.

Thus, compositions of these specimens were determined by measurement of the lattice parameters. A short length cut from the end of each rod was electrochemically thinned to a whisker suitable for mounting in a Debye-Scherrer camera. (That Debye is just everywhere!) Films were corrected for

shrinkage and the lattice parameters were calculated by the method of Vogel and Kempter (26) using the Hess single iteration procedure. The individual results were converted to compositions using my earlier data expressing the relation between lattice parameters, densities and gold content of slowly-cooled alloys (page 2, line 12, herein).

Copper current leads and 0.005 in. tantalum potential leads were spot-welded to the rods. All measurements were taken at a constant 100 mA current by a potentiometric comparison of voltage drops across the specimen and a 0.001 ohm manganin standard resistor. The thermal and contact emf's were averaged by the standard current reversal technique.

The residual resistance was measured by immersion of the sample and several inches of leads in liquid helium. The temperature dependent curves were measured by immersion of the sample in a stirred bath of 2-methyl-pentene-1, which was first frozen in a dewar by a coil containing liquid nitrogen. The specimen, supported on a quartz tube, and with a thermocouple located near the middle of the gauge length, was immersed in the stirred slurry and the ensemble allowed to warm from the freezing point of 137.2°K to about 260°K--a process which took 6-7 hours. Readings were taken every 3-4 degrees, again by comparison and with current reversal. The temperature change of the bath during a reading process, which would take about 20 seconds, was nominally 0.1°K, and an average temperature was assigned to the data point. I was

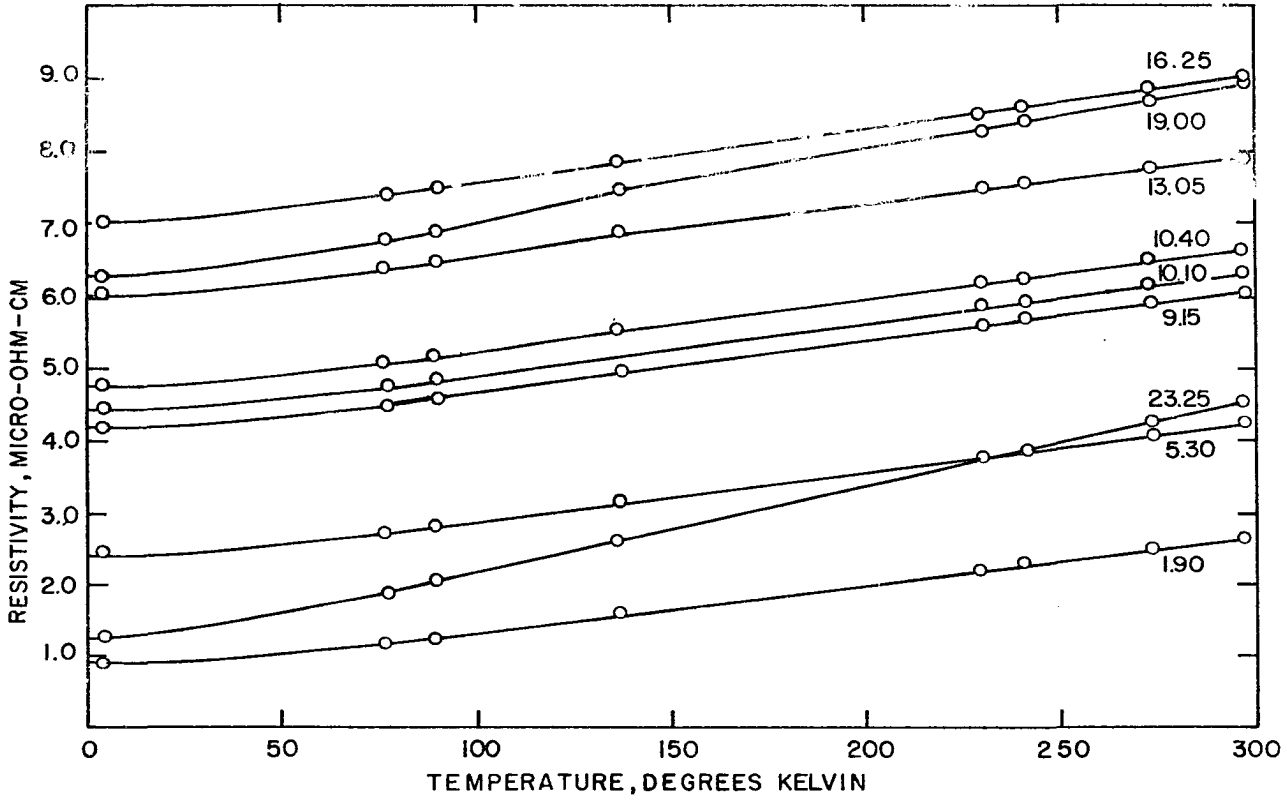


Figure 2. The electrical resistivity of copper-rich, Cu-Au alloys as a function of temperature

very pleased with this neat, albeit smelly, routine, which seems to yield excellent results.

Other fixed point data were taken for several other liquids, among them liquid nitrogen and oxygen, some freons, ice water and room temperature. These are not of particular importance here. All the data are graphically summarized in Figures 2 and 3 and tabulated in Tables 3 and 4.

B. Fitting of the Bloch-Gruneisen Equation

Within the context of the assumptions outlined in Section II., the data for each specimen were fit to the Debye-Gruneisen equation and the resultant θ_R was tabulated. To do this in as analytic a way as possible, I adopted the following procedure (27): differentiate the logarithm of the Bloch-Gruneisen equation with respect to log T and rearrange the results to get

$$\frac{d \log \rho}{d \log T} = \tag{13}$$
$$1 + \left|\frac{d \log G(\theta_R/T)}{d \log (\theta_R/T)}\right| - \frac{d \log \theta_R}{d \log T} \left[2 + \left|\frac{d \log G(\theta_R/T)}{d \log (\theta_R/T)}\right|\right]$$

Now if θ_R is not temperature dependent, we have,

$$\frac{d \log \rho(T)}{d \log T} = 1 + \left|\frac{d \log G(\theta_R/T)}{d \log (\theta_R/T)}\right| \tag{14}$$

The function $G(\theta_R/T)$ is given in terms of a simple polynomial expansion (14).

$$G(x) = 1 + \left| \sum_{i=1}^{\infty} a_i x^{2i} \right| \tag{15}$$

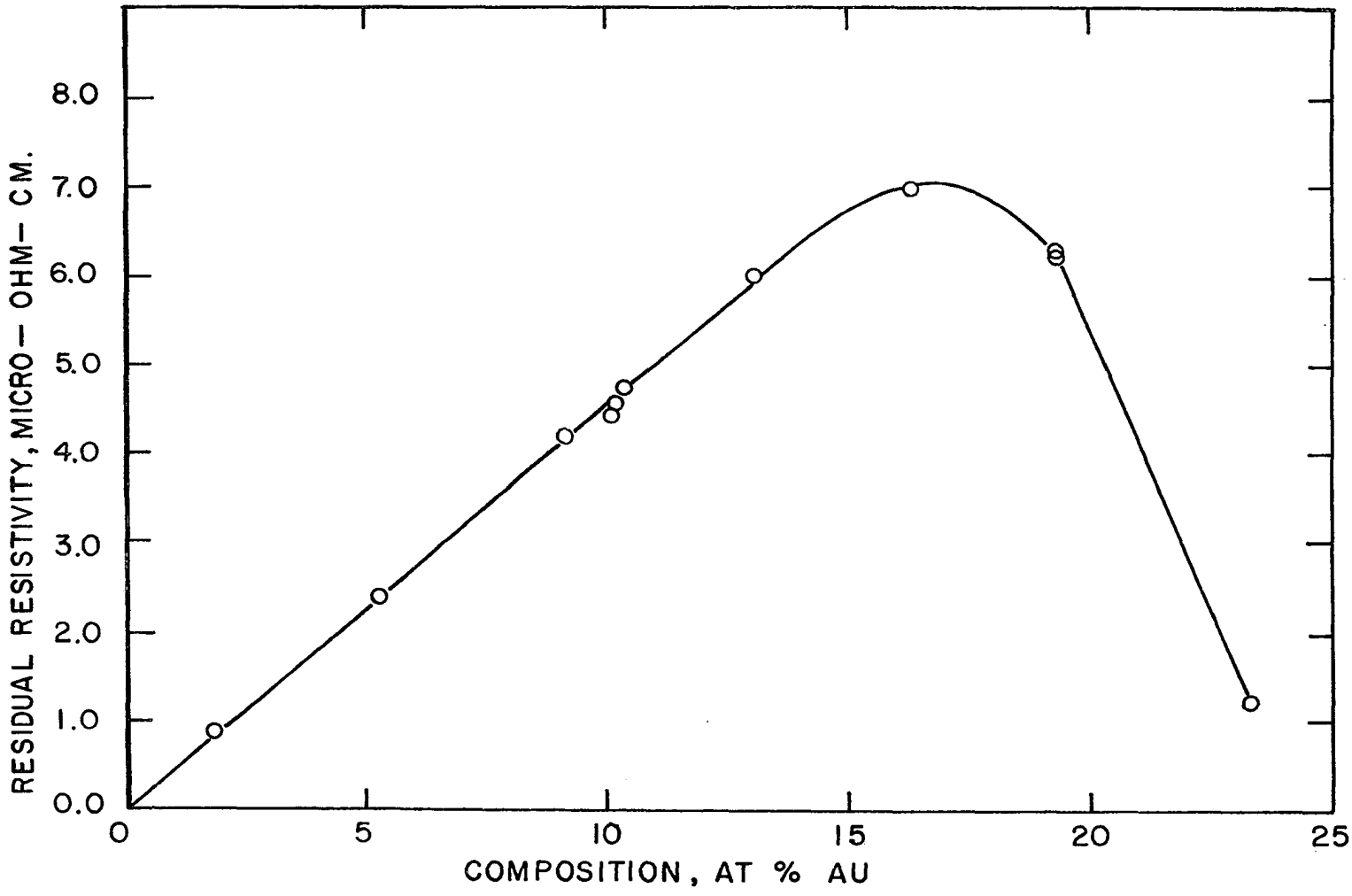


Figure 3. The residual resistivity of copper-rich, Cu-Au alloys as a function of composition

Table 3. Compositions, residual resistivities, and Debye temperatures, θ_R at 150°K, as calculated from Debye-Gruneisen formula for slowly-cooled, copper-rich, Cu-Au alloys

Sample	Lattice parameter (Å)	Composition (at. % Au)	Residual resistivity (micro-ohm-cm)	Debye temperature at 150°C
BC-R-01	3.6677	9.15	4.188	243
BC-R-02	3.6258	1.90	0.918	281
BC-R-03	3.6727	10.20	4.548	228
BC-R-04	3.6721	10.10	4.436	---
BC-R-05	3.6446	5.30	2.435	265
BC-R-06	3.6738	10.40	4.752	---
BC-R-07	3.7065	16.25	7.028	---
BC-R-08	3.7201	19.20	6.279	---
BC-R-09	3.6889	13.05	6.014	204
BC-R-10	3.7380	23.25	1.273	212
BC-R-11	3.7207	19.25	6.287	---
BC-R-12	3.7662	27.35	2.934	---

Table 4. Fixed-point electrical resistivity data for slowly-cooled, copper-rich Cu-Au alloys

Sample	Temperature (°K)							
	4.2	77.4	90.2	137.2	229.0	241.0	273.2	298.0
BC-R-01	4.188	4.488	4.557	4.951	5.563	5.674	5.892	6.059
BC-R-02	0.918	1.184	1.246	1.608	2.214	2.309	2.532	2.698
BC-R-03	4.548	4.879	4.948	-----	5.954	6.052	6.285	6.459
BC-R-04	4.436	4.743	4.812	-----	5.813	5.914	6.143	6.327
BC-R-05	2.435	2.718	2.781	3.152	3.781	3.866	4.098	4.266
BC-R-06	4.752	5.078	5.148	5.528	6.164	6.239	6.488	6.659
BC-R-07	7.028	7.371	7.445	7.849	8.496	8.602	8.855	9.021
BC-R-08	6.279	6.776	6.876	7.428	8.263	8.393	8.680	8.909
BC-R-09	6.014	6.357	6.423	6.855	7.450	7.537	7.786	7.935
BC-R-10	1.273	1.905	2.033	2.657	3.744	3.892	4.282	4.557
BC-R-11	6.287	6.819	6.918	-----	8.299	8.398	8.721	8.938
BC-R-12	2.934	3.653	3.767	4.395	5.434	5.561	5.935	6.214

and for the first seven terms

$$a_1 = -5.55555 \times 10^{-2}$$
$$a_2 = 2.0833 \times 10^{-3}$$
$$a_3 = -6.6138 \times 10^{-5}$$
$$a_4 = 1.9290 \times 10^{-6}$$
$$a_5 = -5.368 \times 10^{-8}$$
$$a_6 = 1.435 \times 10^{-9}$$
$$a_7 = -3.866 \times 10^{-11}$$
$$a_8 = 1.017 \times 10^{-12} \qquad (16)$$

Using this, a computer-calculated table of the right-hand side of equation 14 was produced for $0.050 \leq \theta_R/T \leq 3.050$.

The left-hand side of equation 14 was evaluated by fitting the temperature dependent resistance data to an arbitrary polynomial which adequately described the slopes and curvatures in the 140°K-260°K range of interest. This polynomial and its coefficients, which have no physical significance, were used to calculate a smooth series of values of the left-hand side of this equation at each measured temperature point. Comparison of each of these values with the computer-calculated table mentioned above yielded θ_R/T values and then the factor θ_R. If this θ_R varied little or not at all over the temperature range, thus satisfying the basic assumption of this method, I accepted it as being characteristic of the composition under consideration. In this way a series of θ_R's for the dilute alloys was generated. A θ_R sufficiently independent of temperature was not found for alloys of greater

than ~15% gold content. For other alloys, a value of θ_R at 150°K is tabulated in Table 3. Discussion of these results is deferred until Section III., where it will be presented together with the calculations of θ_D from elastic moduli.

IV. MEASUREMENT AND INTERPRETATION OF ELASTIC CONSTANTS

...This electric force, that keeps a thousand pulses dancing.

Tennyson - In Memoriam

A. Experimental Procedure

As discussed in Section II., the elastic moduli provide a good basis for calculation of the Debye temperatures because they are related to the velocity of sound waves in the media. The particular method used here involves measurement of the ultrasonic velocities of acoustic waves propagated in single crystals of the alloys.

The single crystals were prepared by melting appropriate amounts of copper and gold in an outgassed, pointed, graphite or zirconia crucible and lowering the crucible and its contents through a temperature gradient in the classic Bridgman method. For the case of partial mixing, the middle of the ingot should have relatively small concentration gradients, so the samples were cut by electrospark erosion from the center of the subsequently oriented single crystals. The composition gradient was checked by electron microprobe analysis on one such alloy and found to be negligible.

These specimens were heat-treated similarly to the resistivity specimens, and the history of the samples can be summarized as follows:

1. grown under vacuum (1×10^{-3} torr) by the Bridgman

method,

2. homogenized for 10 days at 900°C under a vacuum of 10^{-6} torr,
3. cooled from 450°C to 150°C in a period of 100 days in a vacuum better than 1 x 10^{-7} torr.

The lattice parameters of each specimen were measured by using Mo radiation on a diffractometer. By irradiating the (110) face, three orders of diffracted beams could be received for α_1, α_2, β_1 and β_2 wavelengths. The lattice parameter was calculated using the method of Vogel and Kempter (26), with a cos θ cot θ extrapolation function. These lattice parameters were used to determine the concentration of each sample, again using the results of my previous investigation (page 2, line 12, herein). The results are shown in Table 5.

Table 5. Physical parameters of Cu-Au elastic constant specimens

Crystal	Lattice parameter (Å)	Composition (at. % Au)	Density at 25°C, ($gms./cm^3$)	Thickness at 25°C (cm)
4	3.637	3.95	9.48	0.6290
9	3.665	8.85	10.16	0.4210
5	3.696	14.28	10.84	0.8295
6	3.718	18.70	11.45	0.7721
10	3.739	23.45	12.02	0.8765

Sample thicknesses were measured by a micrometer and were corrected for thermal expansion by interpolating the results

of Nix and MacNair for pure Cu (28) and Flinn et al. for Cu_3Au (3). Data from 77°K to about 250°K were obtained by submersion in or suspension over a boiling liquid nitrogen bath; data from 4.2°K to about 70°K by a similar method with liquid helium; additional points at room temperature and with the specimen and holder buried in crystalline ice complete the curve. Data points were recorded at intervals no greater than 20 Kelvin degrees apart and a smooth curve drawn through the resultant transit times. Copper-constantan thermocouples were used to monitor the temperature from 40°K to 300°K; Au-0.03% Fe vs. normalized Ag thermocouples were used in the 4.2°K-40°K range. The transducers were bonded to the crystal faces with Salol (phenyl salicylate) for the shear modes in the 250°K-300°K range; nonaqueous stopcock grease was used for all other temperatures and propagation modes.

The experimental technique for the pulse-superposition measurement of ultrasonic velocities is due to McSkimin (29), and depends on the propagation and successive reflection of an r.f. pulse package in a square wave envelope between parallel faces of the specimen. Various authors, McSkimin included (29-31), have attempted to evaluate some of the errors associated with this method. I would like to express my thoughts and calculations for two of these: bond transit time error and crystal misorientation errors.

B. Analysis of Errors

McSkimin evaluated the transit time error induced at the

transducer-bond-specimen interface by an electrical engineering analogue with a transmission line of different impedences. This indicates correction of ~0.005-0.010 microseconds should be subtracted from the total transit time to give the transit time in the crystal only. The few rough empirical attempts to evaluate this have indicated errors of $\geq$ 0.1 microsecond magnitude (32-34). My own philosophy is that very carefully prepared bonds, on carefully prepared, flat specimen surfaces, induce little error (0.05 microseconds magnitude) into the indicated transit times. For large crystals (~1.0 cm) this is less than 1% or so and cannot be said to be appreciable.

Methods of handling place an upper level on the precision with which a crystal may be sliced parallel to a specified plane. Small, random errors will be incurred in the Laue camera, cutting device and final surface preparations. Subgrains also add to the problem. Waterman has used a continuum model to derive equations giving velocity changes for various misorientations (35). The graphs of some of the formula for various cubic materials are shown in Figures 4-6. The vocabulary is explained in Waterman's analysis. Suffice it to say, that under the model presumed and for misorientations of less than two degrees from the [110] axis, the velocity (hence transit times) will be less than 0.5% in error for all propagation modes.

These two errors, plus those due to composition gradients, density determination, length measurement capabilities and

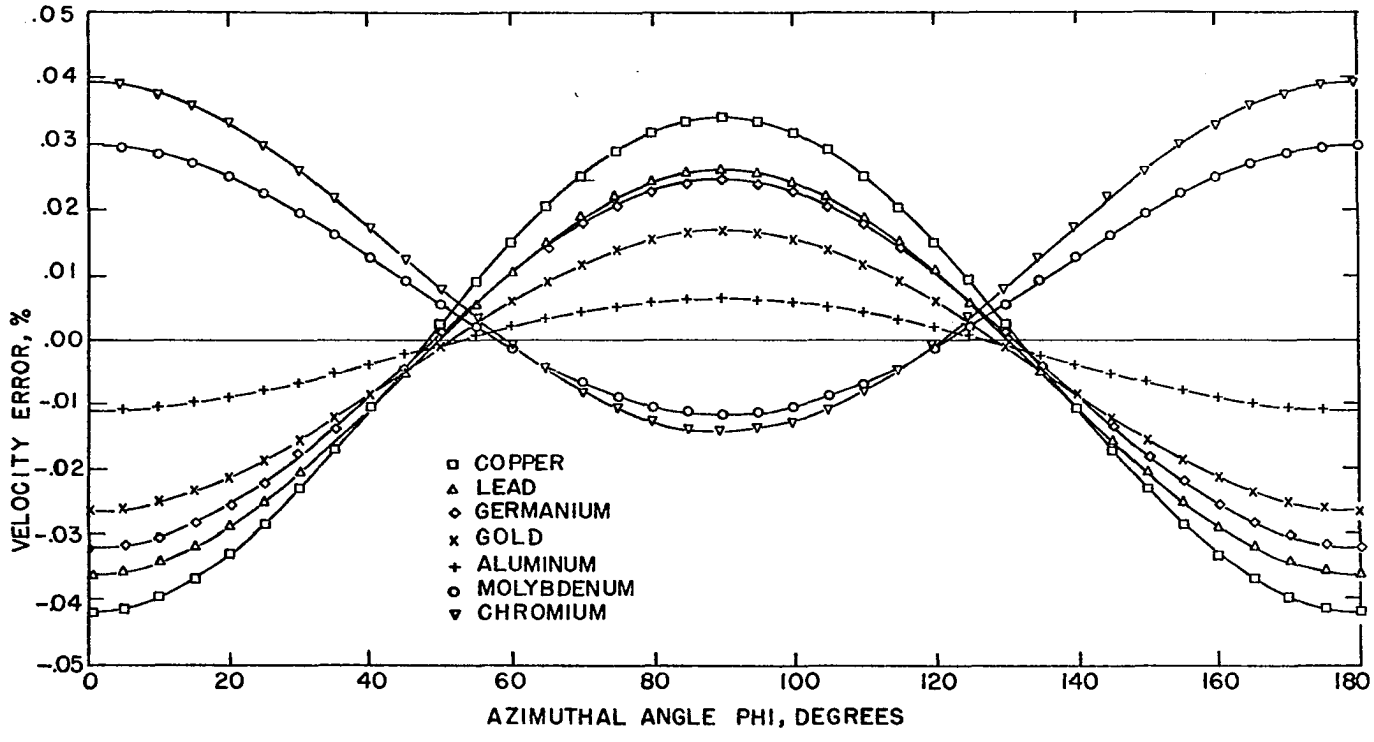


Figure 4. The percentage error in the velocity of the longitudinal wave, ΔV_L, for a polar misorientation of two degrees as a function of azimuthal angle for several cubic metals

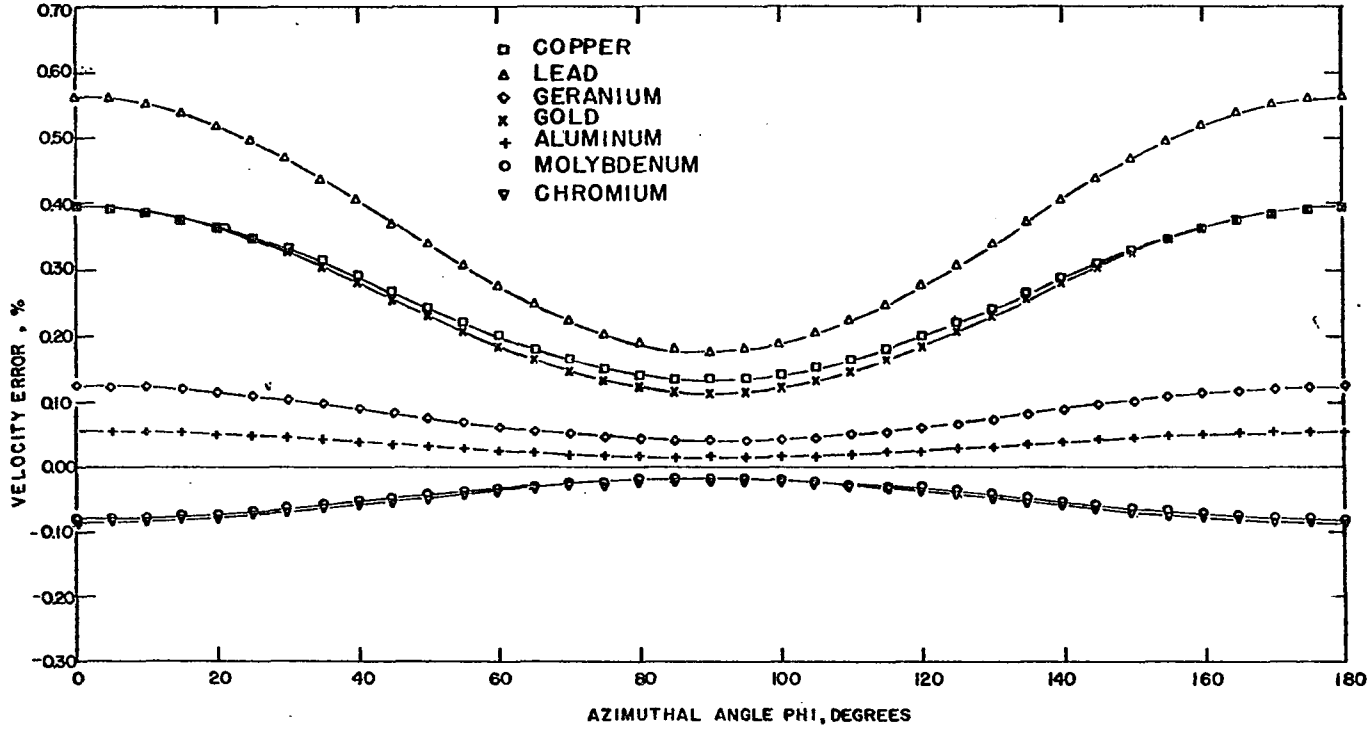


Figure 5. The percentage error in the velocity of the transverse wave, ΔV, for a polar misorientation of two degrees as a function of azimuthal angle for several cubic metals

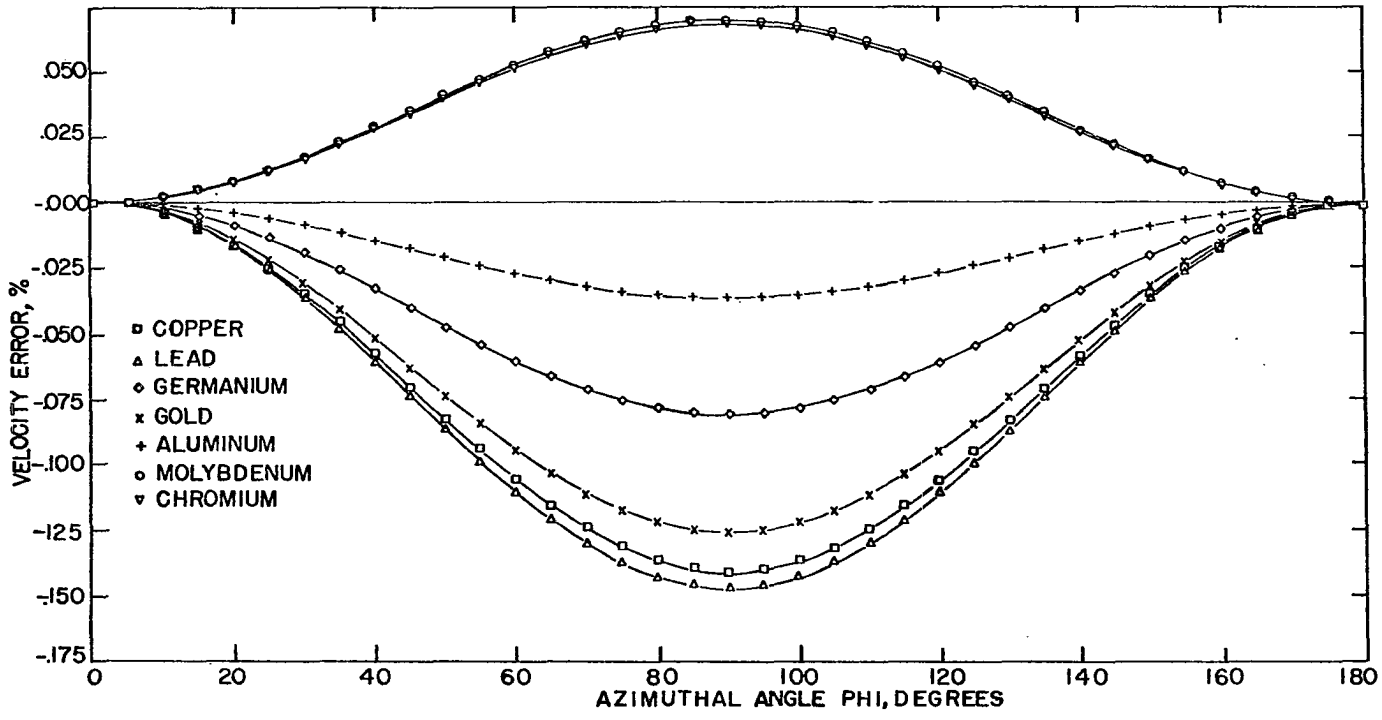


Figure 6. The percentage error in the velocity of the transverse wave, $\Delta V'$, for a polar misorientation angle of two degrees as a function of azimuthal angle for several cubic metals

other small sources of experimental error, will add up to at most 2% total error, and probably less. But with present limitations on the state of the art, it seems absurd to claim any better than 1% accuracy, or more than three significant figures in the presentation of results.

With this in mind, the reader is directed to Table 6 and Figures 7-12 where the composition and temperature dependences of the bulk moduli, K, $C_L = \frac{1}{2}(C_{11} + C_{12} + 2C_{44})$, the Fuchsian shear moduli, C and C', which are later analyzed, and the isotropy ratio, S, are presented.

The errors mentioned above are presumed to be the source of the "anomalous" temperature dependence of the bulk modulus, particularly for the 14.28% and 18.70% specimens, which exhibit slight variance from the monotonic decrease expected with rising temperature. It is quite likely that slight changes in the character of the bond in any one or all of the three measured transit times could result in slight deviations from the true value--a deviation which appears to affect the third decimal place in the bulk modulus. However, this amounts to an error of less than 0.5% and is not critical to a realistic interpretation of the data.

The salient features of these results can be summarized by noting that the moduli all suffer sharp decreases as the gold content is increased from zero, followed by some degree of increase as the gold content reaches a level at which some degree of long-range ordering can take place.

Table 6. Adiabatic elastic constants, m units of 10^{12} dynes/cm^2, and isotropy of slowly-cooled, copper-rich, Cu-Au alloys

Composition (at. % Au)	Temperature (^{o}K)	C_L	C	C'	K	S
0.00[a]	0.	2.323	0.818	0.256	1.420	0.314
	50.	2.318	0.815	0.256	1.418	0.314
	100.	2.302	0.806	0.253	1.412	0.314
	150.	2.278	0.794	0.250	1.403	0.314
	200.	2.256	0.782	0.245	1.393	0.313
	250.	2.230	0.768	0.240	1.382	0.312
	300.	2.203	0.754	0.235	1.371	0.312
3.95	0.	2.163	0.745	0.241	1.337	0.324
	50.	2.153	0.741	0.239	1.332	0.322
	100.	2.136	0.732	0.235	1.325	0.321
	150.	2.119	0.724	0.231	1.318	0.319
	200.	2.099	0.713	0.226	1.310	0.317
	250.	2.074	0.701	0.222	1.299	0.316
	300.	2.048	0.689	0.218	1.286	0.316
8.85	0.	1.979	0.716	0.234	1.184	0.327
	50.	1.971	0.713	0.233	1.181	0.326
	100.	1.963	0.706	0.229	1.178	0.324
	150.	1.945	0.697	0.224	1.173	0.322
	200.	1.923	0.685	0.220	1.164	0.320
	250.	1.902	0.675	0.215	1.155	0.318
	300.	1.882	0.664	0.210	1.148	0.316

[a]Overton and Gaffney (33)

Table 6. (Continued)

Composition (at. % Au)	Temperature (°K)	C_L	C	C'	K	S
14.28	0.	1.950	0.708	0.231	1.165	0.327
	50.	1.948	0.705	0.230	1.167	0.326
	100.	1.940	0.697	0.227	1.168	0.325
	150.	1.923	0.686	0.222	1.163	0.324
	200.	1.902	0.675	0.217	1.155	0.322
	250.	1.875	0.663	0.213	1.141	0.321
	300.	1.849	0.649	0.208	1.130	0.321
18.70	0.	1.969	0.715	0.238	1.174	0.333
	50.	1.966	0.712	0.236	1.174	0.332
	100.	1.954	0.703	0.232	1.174	0.330
	150.	1.939	0.692	0.228	1.171	0.330
	200.	1.918	0.681	0.224	1.163	0.329
	250.	1.890	0.670	0.219	1.147	0.327
	300.	1.862	0.659	0.215	1.131	0.326
23.45	0.	2.080	0.726	0.258	1.268	0.355
	50.	2.077	0.723	0.257	1.268	0.355
	100.	2.062	0.715	0.253	1.263	0.354
	150.	2.041	0.705	0.249	1.254	0.353
	200.	2.020	0.694	0.244	1.245	0.351
	250.	1.993	0.682	0.239	1.231	0.350
	300.	1.954	0.671	0.234	1.206	0.349
24.90[b]	4.2	2.342	0.736	0.287	1.510	0.390

[b]Flinn, McManus and Rayne (3)

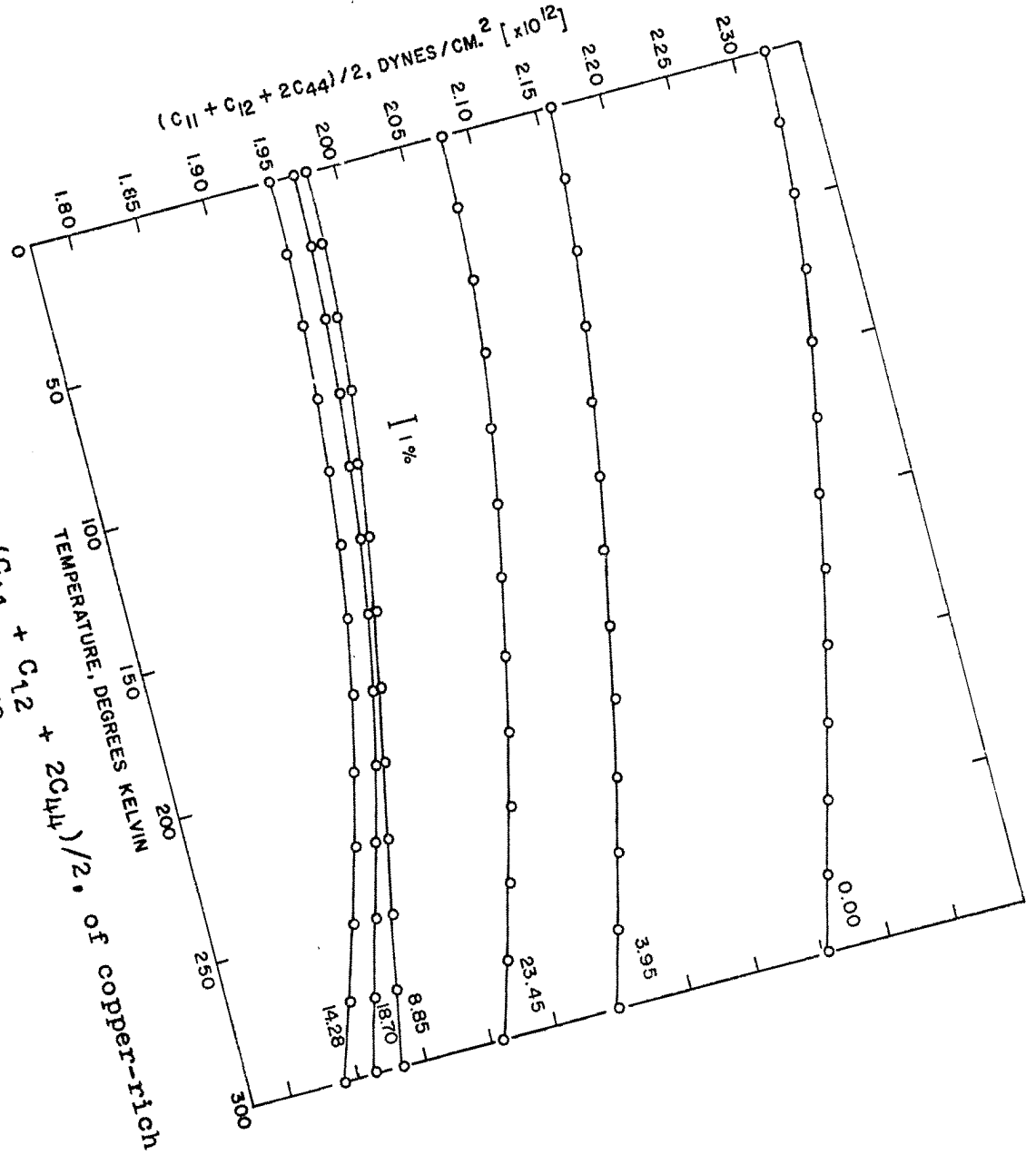


Figure 7. The elastic modulus $C_L = (C_{11} + C_{12} + 2C_{44})/2$, of copper-rich, Cu-Au alloys as a function of temperature

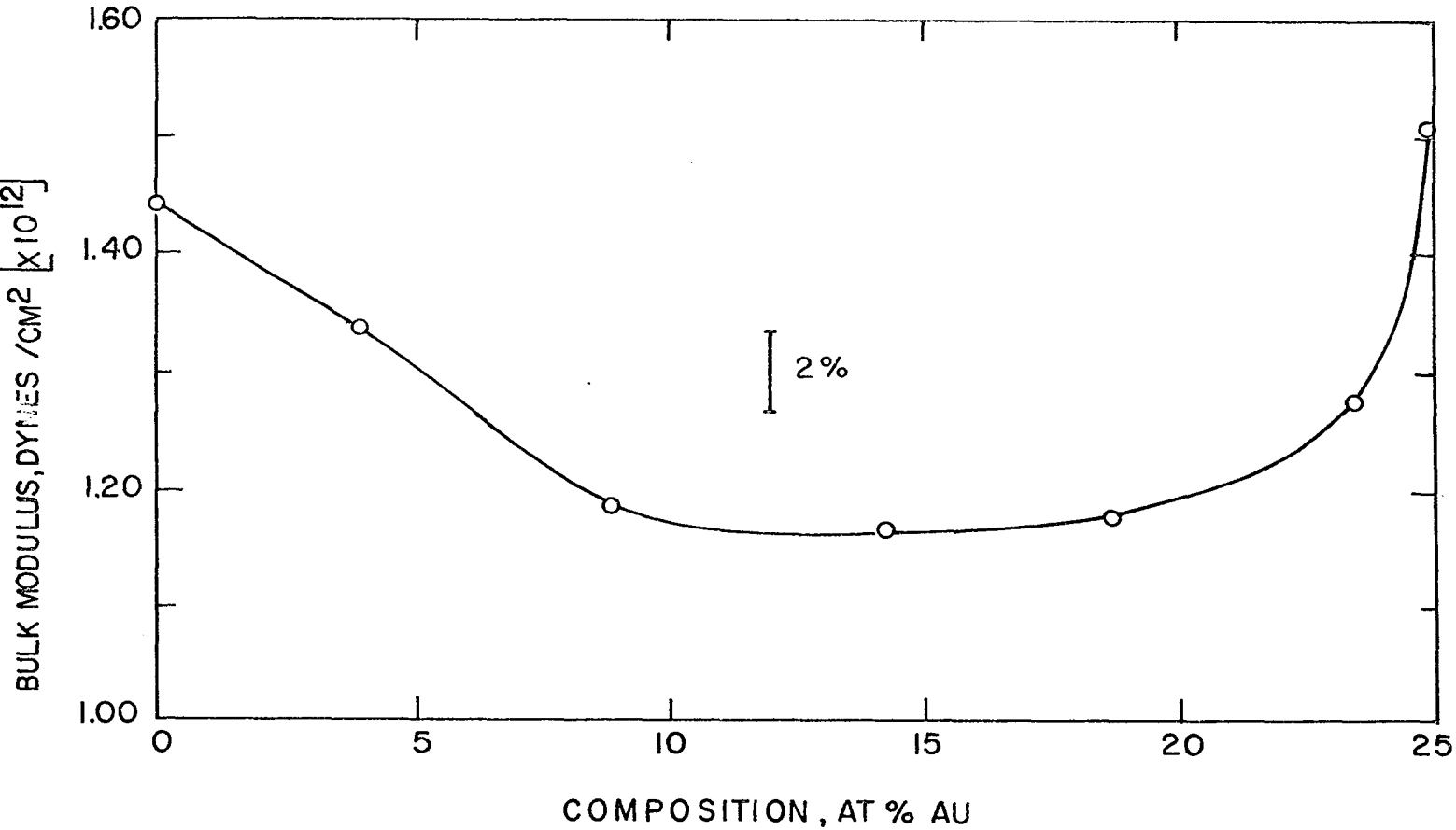


Figure 8. The bulk modulus, $(C_{11} + C_{12})/3$ at 0°K, of copper-rich, Cu-Au alloys as a function of composition

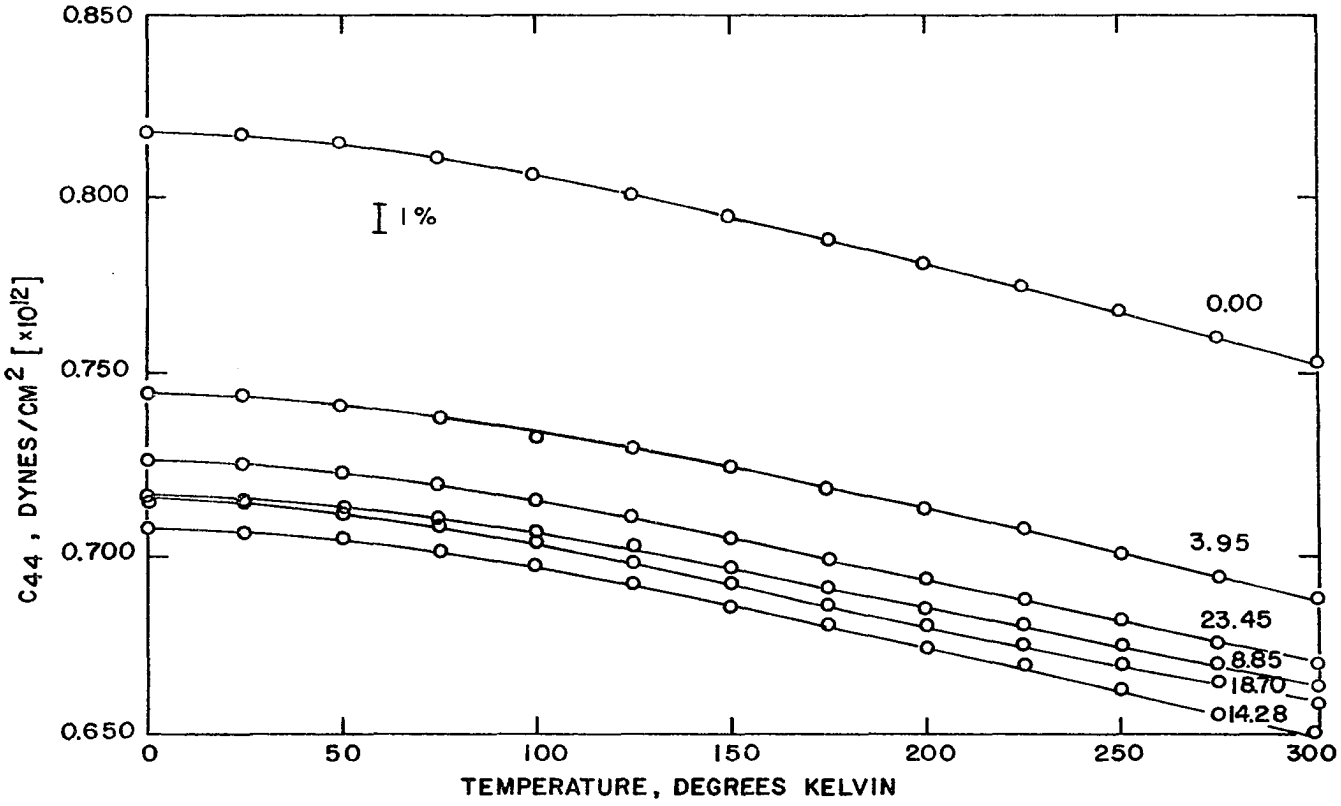


Figure 9. The elastic modulus $C = C_{44}$ of copper-rich, Cu-Au alloys as a function of temperature

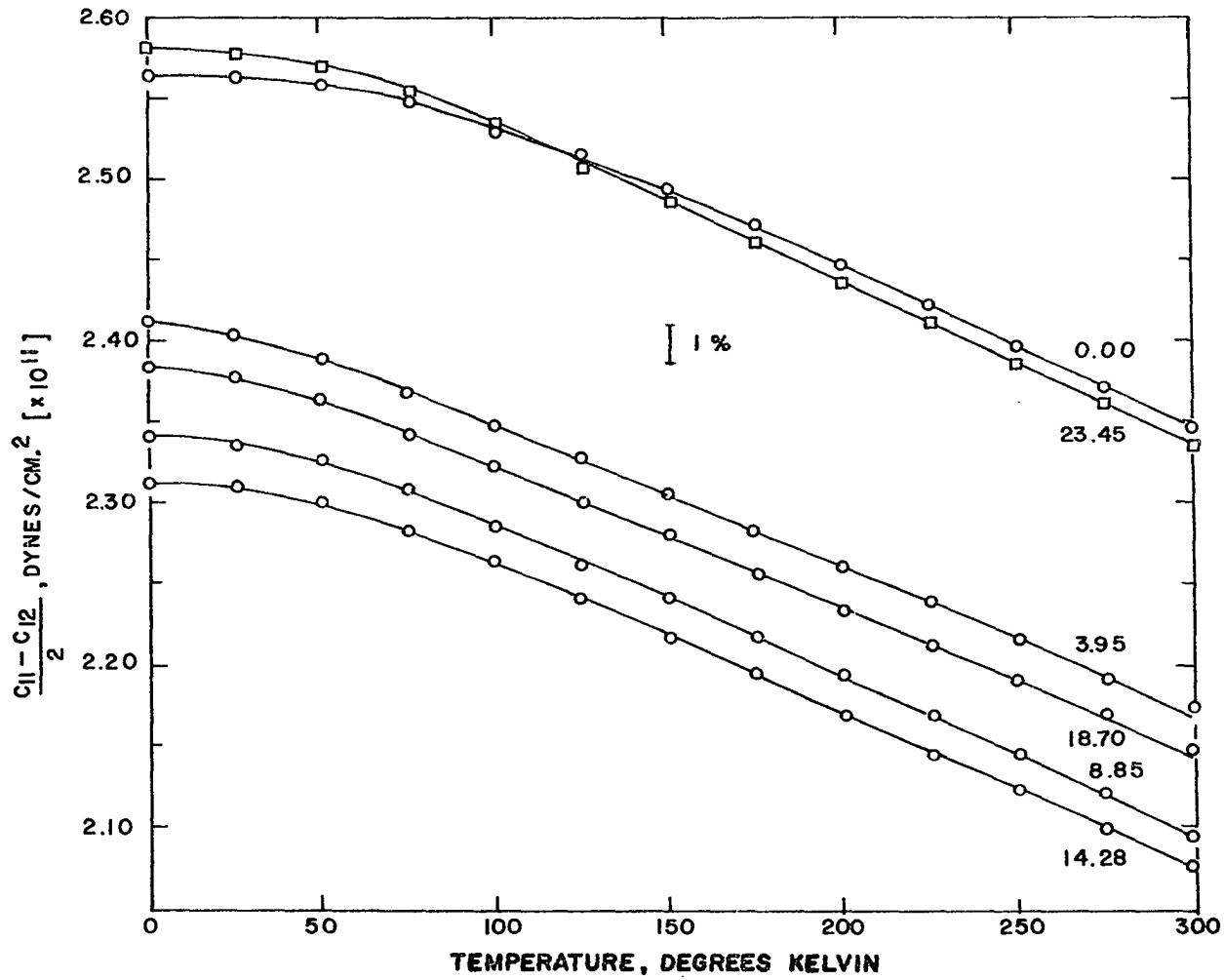
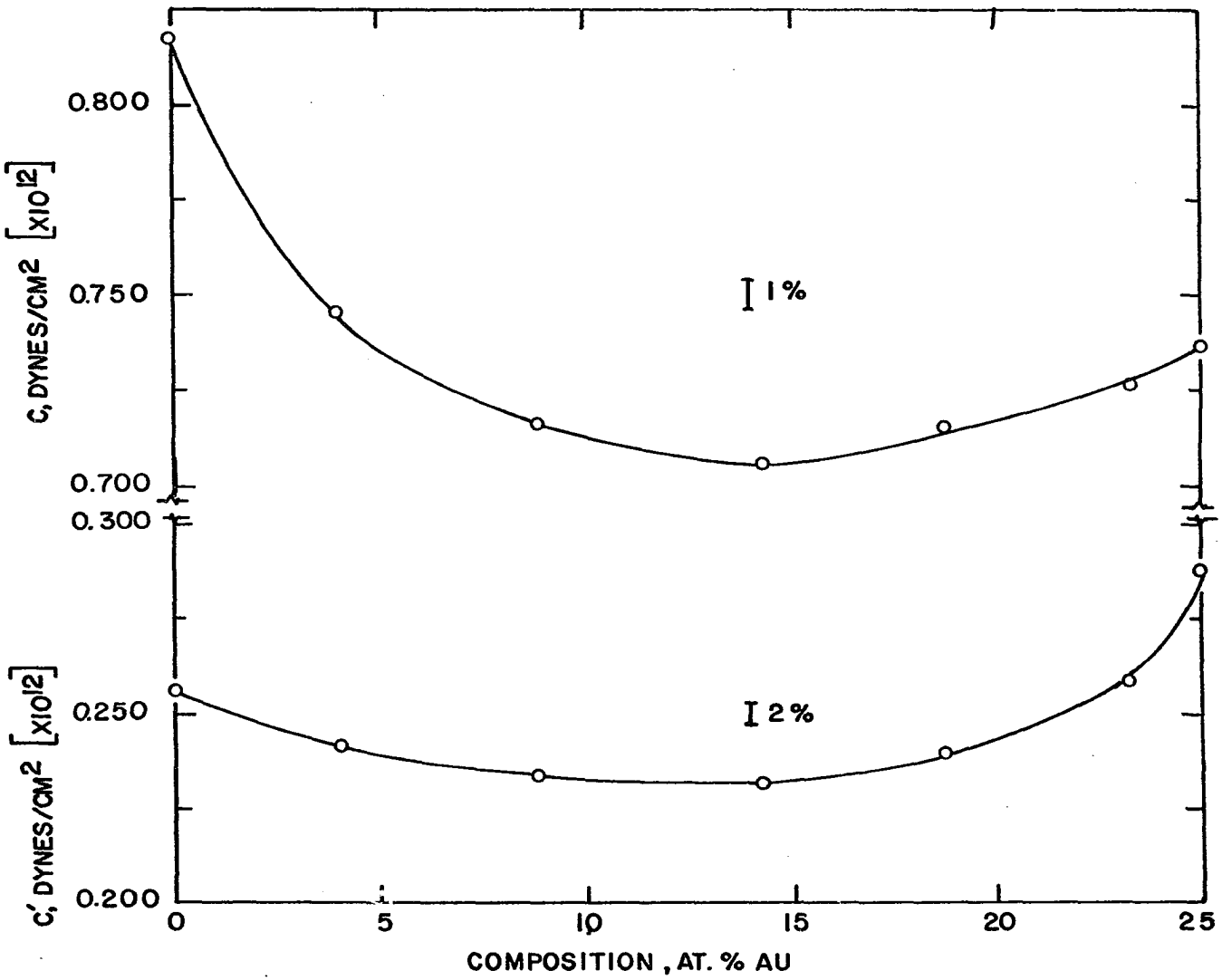


Figure 10. The elastic modulus $C' = (C_{11} - C_{12})/2$, of copper-rich, Cu-Au alloys as a function of temperature

Figure 11. The elastic moduli, $C = C_{44}$ and $C' = (C_{11} - C_{12})/2$ at $0^{\circ}K$, of copper-rich Cu-Au alloys as a function of composition


0.800
0.750
0.700
0.300
0.250
0.200
C, DYNES/CM2 [X10I2]
C', DYNES/CM2 [X10I2]
I 1%
I 2%
0
5
10
15
20
25
COMPOSITION , AT. % AU

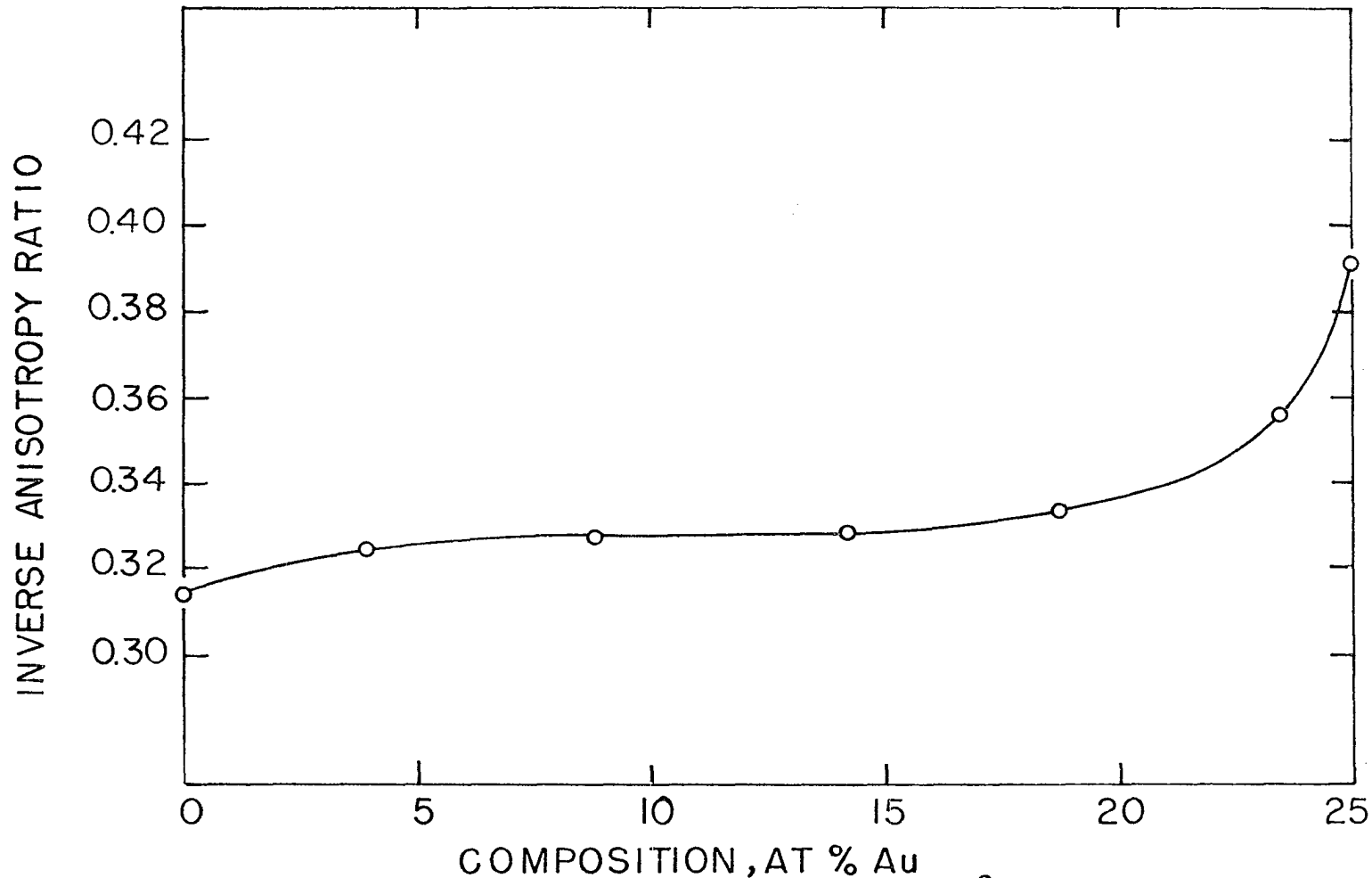


Figure 12. The elastic isotropy, $S = (C_{11} - C_{12})/2C_{44}$ at $0^{\circ}K$, of copper-rich, Cu-Au alloys as a function of composition

C. Calculation and Analysis of θ_{el} and θ_R

This rather unexpected behavior notwithstanding, the calculation of the Debye temperatures by the method of de Launay is straightforward, and the results are shown in Figures 13 and 14 and Table 7. Since, in this case, the integration can almost always be performed, there is no composition region in which a characteristic temperature cannot be defined. A method of interpolation, also designed by de Launay was used in this calculation (36).

In the dilute range, the results here parallel the results from the Debye-Gruneisen analysis of Section II.--insofar as they go. The behavior in the dilute region is characterized by a steep decrease as the gold content increases. This negative slope is considerably smaller than that expected from a strictly linear interpolation between the pure elements, as can be seen in Figure 14. Such a behavior becomes the verification of the second part of my hypothesis--that the vibrational spectra undergoes large changes as the gold content increases. From this limited amount of information we cannot particularize, for as you may remember from Section II., the Debye temperature is the "...phenomenological parameter defining the limits of the parabolic representation which best describes the vibrational spectrum under the conditions of averaging of the particular method."

Indeed, it appears that those aspects of the vibrational spectra which bear on the scattering of electrons and so con-

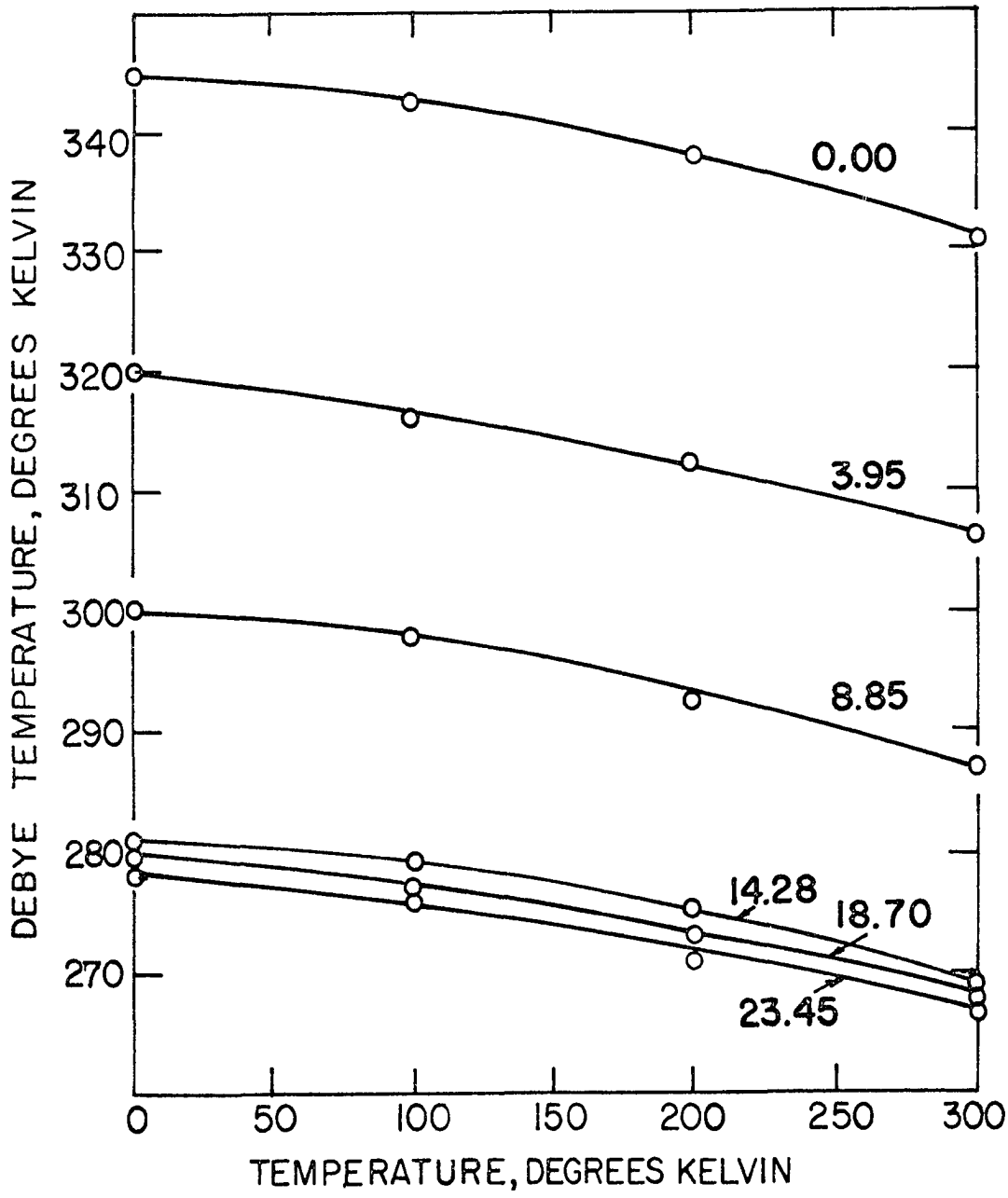


Figure 13. The Debye temperatures of copper-rich, Cu-Au alloys calculated from the elastic moduli as a function of temperature

Figure 14. The Debye temperatures of copper-rich, Cu-Au alloys calculated from elastic moduli and the Bloch-Gruneisen formula as a function of composition

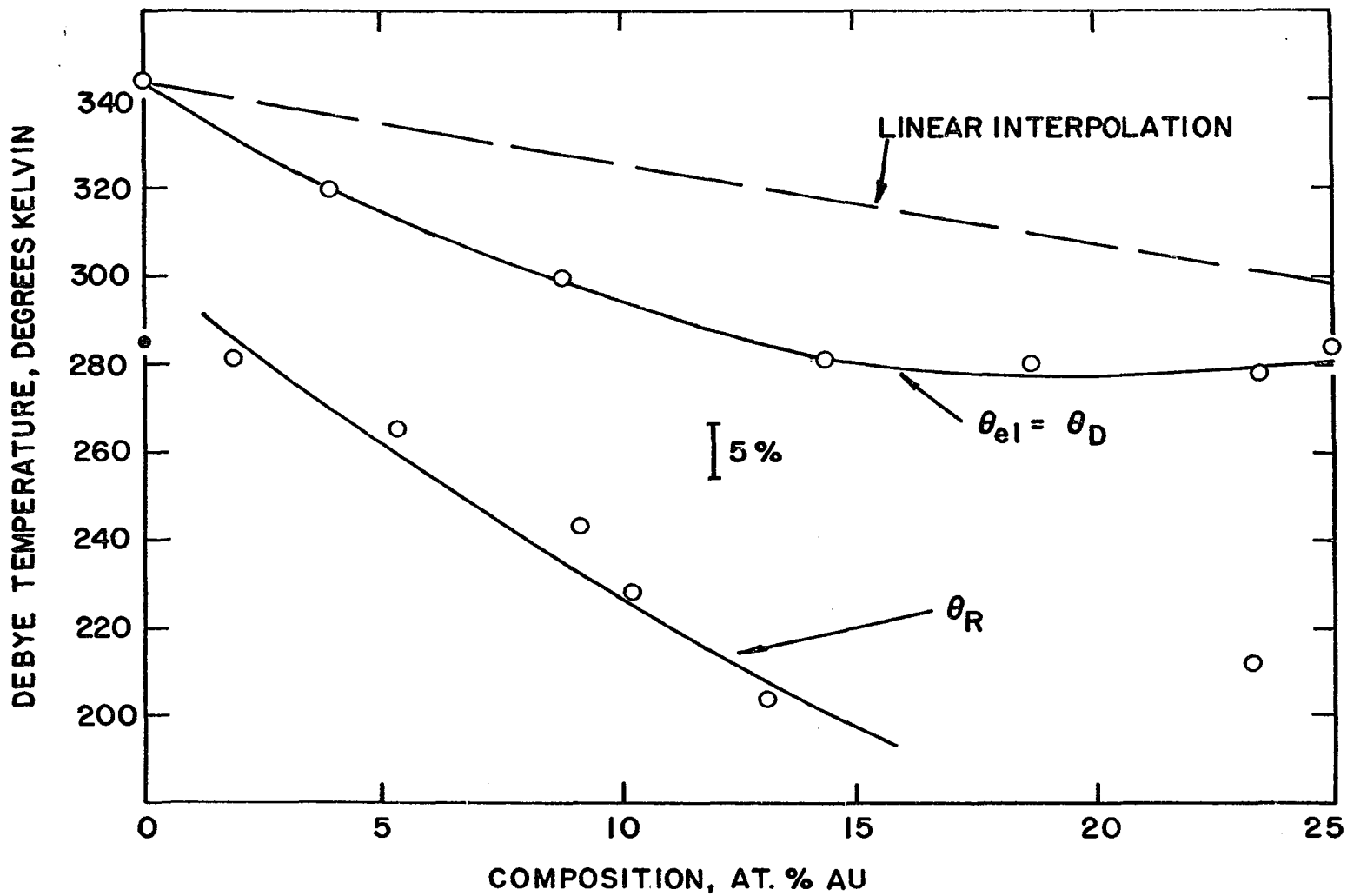

DEBYE TEMPERATURE, DEGREES KELVIN
340
320
300
280
260
240
220
200
0
5
10
15
20
25
COMPOSITION, AT. % AU
LINEAR INTERPOLATION
$\theta_{el} = \theta_D$
5%
θ_R

Table 7. Debye temperatures (Θ_{el}) calculated from the elastic moduli of copper-rich, Cu-Au alloys

Composition (at. % Au)	Average mass per atom (gms./mole)	Temperature (^{o}K)	Debye Temperature (^{o}K)
0.00[a]	63.54	0.0	345
		100.0	343
		200.0	337
		300.0	331
3.95	68.82	0.0	320
		100.0	316
		200.0	312
		300.0	306
8.85	75.35	0.0	300
		100.0	298
		200.0	293
		300.0	287
14.28	85.60	0.0	281
		100.0	279
		200.0	275
		300.0	269
18.70	88.50	0.0	280
		100.0	277
		200.0	273
		300.0	268
23.45	94.83	0.0	278
		100.0	276
		200.0	271
		300.0	267
24.90[b]	94.40	4.2	284

[a]Overton and Gaffney (33)

[b]Flinn, McManus and Rayne (3)

tribute to the thermal component of the electrical resistance are becoming so variable around 15% Au that a θ_R cannot be defined. However, as the ordered composition Cu_3Au is approached, the situation seems to improve and a value of $\theta_R = 218^\circ K$ seems to apply at $150^\circ K$. This differs from the value of $197^\circ K$ recorded by Bowen at $75^\circ K$ (22), but the difference is in the proper direction for a more fully ordered alloy tested at a higher temperature.

As mentioned in Section II., according to the Bloch theory, only longitudinal waves (phonons) should interact with the electrons giving rise to electrical resistance (23). Accordingly, we should expect some correlation between V_L, the velocity of the longitudinal waves, and θ_R. For materials of cubic symmetry, $V_L = (C_{11}/\rho)^{1/2}$, and for isotropic media

$$\theta_L = \left(\frac{h}{k}\right) V_L \left(\frac{3}{4\pi V_a}\right)^{1/3}$$

$$= 4.708 \times 10^{-11} \left(\frac{C_{11}}{\rho}\right)^{1/2} \frac{1}{a} \qquad (17)$$

where V_a is the volume of an atom and a is the lattice parameter.

Although these Cu-Au alloys are not elastically isotropic, the context of the theory is sufficiently approximate that we may look for basic behavioral agreement. In fact, the behavioral agreement is good, as shown in Table 8 and Figure 15. The fact that the absolute values are in obvious disagreement is true for all metals. Blackman and others have met with no

Table 8. Empirical and theoretical Debye temperatures used in the Bloch-Gruneisen formulation of the electrical resistance of Cu-Au alloys

Empirical			Theoretical			
Composition (at. % Au)	Debye temperature (^{o}K)	C_{11} (10^{12} dynes/cm^2)	Density (gms./cc)	Azero	Composition (at. % Au)	Calculated Debye temperature (^{o}K)
0.00[a]	320	1.735	9.03	3.607	0.00	572
1.90	281	1.659	9.58	3.628	3.95	538
5.30	265	1.497	10.27	3.656	8.85	502
9.15	243	1.473	10.96	3.686	14.28	470
10.20	228	1.492	11.56	3.709	18.70	456
23.25	212					

[a]Kelly (20)

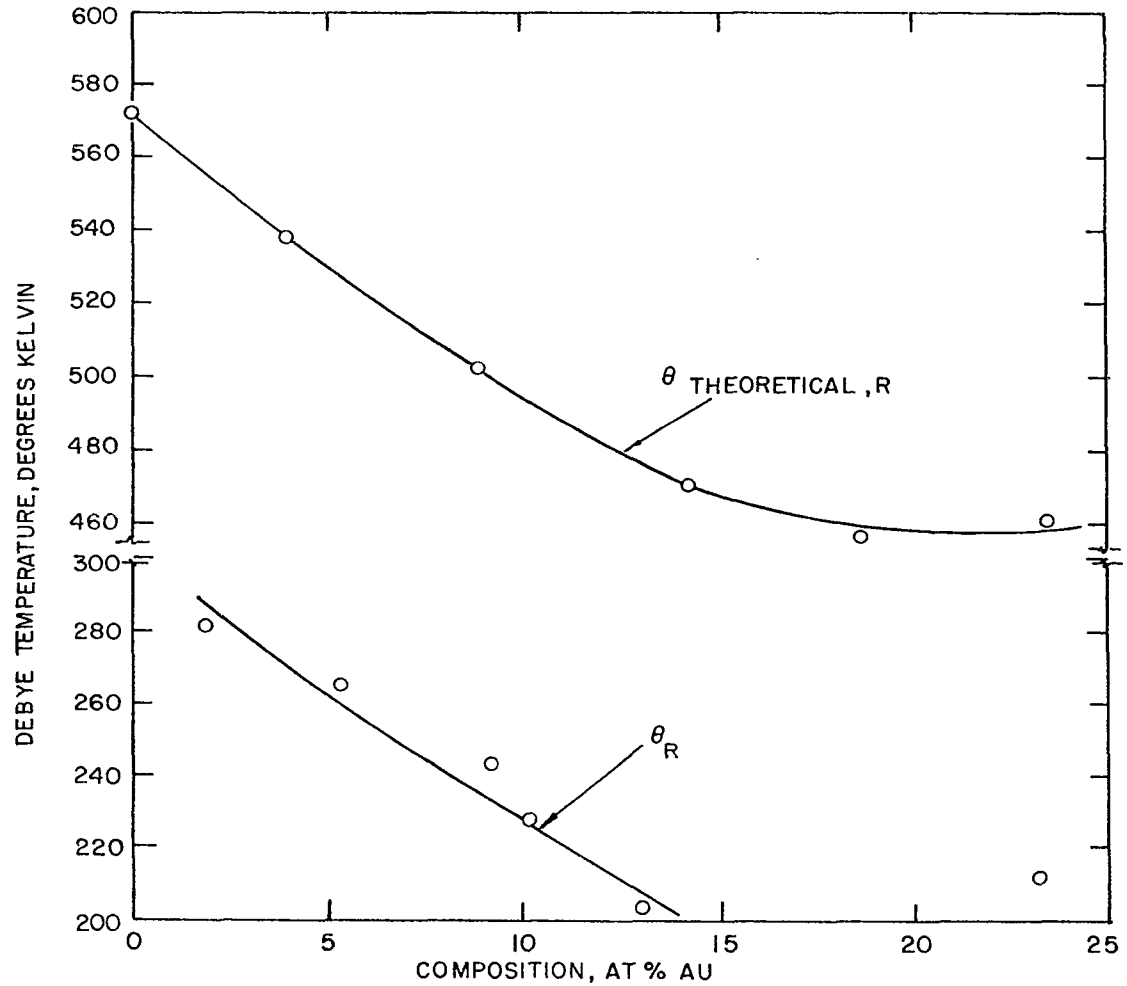


Figure 15. The empirical and theoretical Debye temperatures calculated from the Bloch-Gruneisen formula and longitudinal wave phonon interaction process respectively, as a function of composition

success in trying to rationalize this fact; their obvious conclusion is that the transverse waves must play a part in the resistance also. Consequently, I can only point out that there is parallel behavior between V_L and θ_R, but that this does not necessarily imply that only longitudinal waves give rise to the electrical resistance of Cu-Au alloys.

The Debye temperatures calculated from the elastic constants of off-stoichiometric Cu_3Au compositions are nearly independent of composition. However, rationalization of that fact is difficult, because, as mentioned before, alloys in this region consist of long-range ordered domains in a nearly disordered matrix.

In summary, the sharp decrease of θ_D's and θ_R's in the dilute range is a most important and interesting feature. This, perhaps, implies a large rearrangement in the phonon spectra, possibly due to changes in the internal strains. It is known that there are measurable static displacements in CuAu alloys. Webb has evaluated these by X-ray diffraction peak intensity measurements in quickly cooled powders (21). He found displacements of about 2.5% of the interatomic distance for a 15% Au in Cu sample. I would expect displacements of an even larger percentage for near-equilibrium alloys.

D. Calculation of Vibrational Entropy

In turn, the value of the Debye temperatures provides a good basis for the calculation of ΔS_{vib}, the vibrational con-

tribution to the entropy of mixing. This factor is due to the randomness of the vibrations of the atomic species in the alloys. The equation for S can be expanded in a series:

$$S = R(4 - 3\ln y + \frac{3y^2}{40} - \frac{3y^4}{2240} - \frac{y^6}{36,288} - \frac{y^8}{1,689,000} + ..) \quad (18)$$

where $y = \theta_D/T$.

By first calculating S for the alloy of composition x, and for the pure species, we can calculate

$$\Delta S_{vib}(x) = S_{alloy}(x) - (1 - x)S_{Cu} - xS_{Au} \quad (19)$$

Using the 0^oK values of θ_D, ΔS_{vib} was evaluated for a range of temperatures between 0^oK and 500^oK. The results are displayed in Figure 16 for $T = 300^oK$.

For Cu-Au alloys, the only two important contributions to the entropy of mixing should be vibrational and configurational. For pure species and highly ordered superlattices and phases, the configurational contribution should be zero. Likewise, where there are no static displacements or other forms of internal strains, as will be the case for ordered alloys and phases, the vibrational contribution should be zero. Consequently, Olander (tacitly neglecting electronic and magnetic effects (which may be large)) suggested that ΔS for ordered alloys should exhibit a large cusp in the neighborhood of the stoichiometric composition (37). Although no mathematical representation of the exact configurational entropy is available, we may assume it approximates the ideal

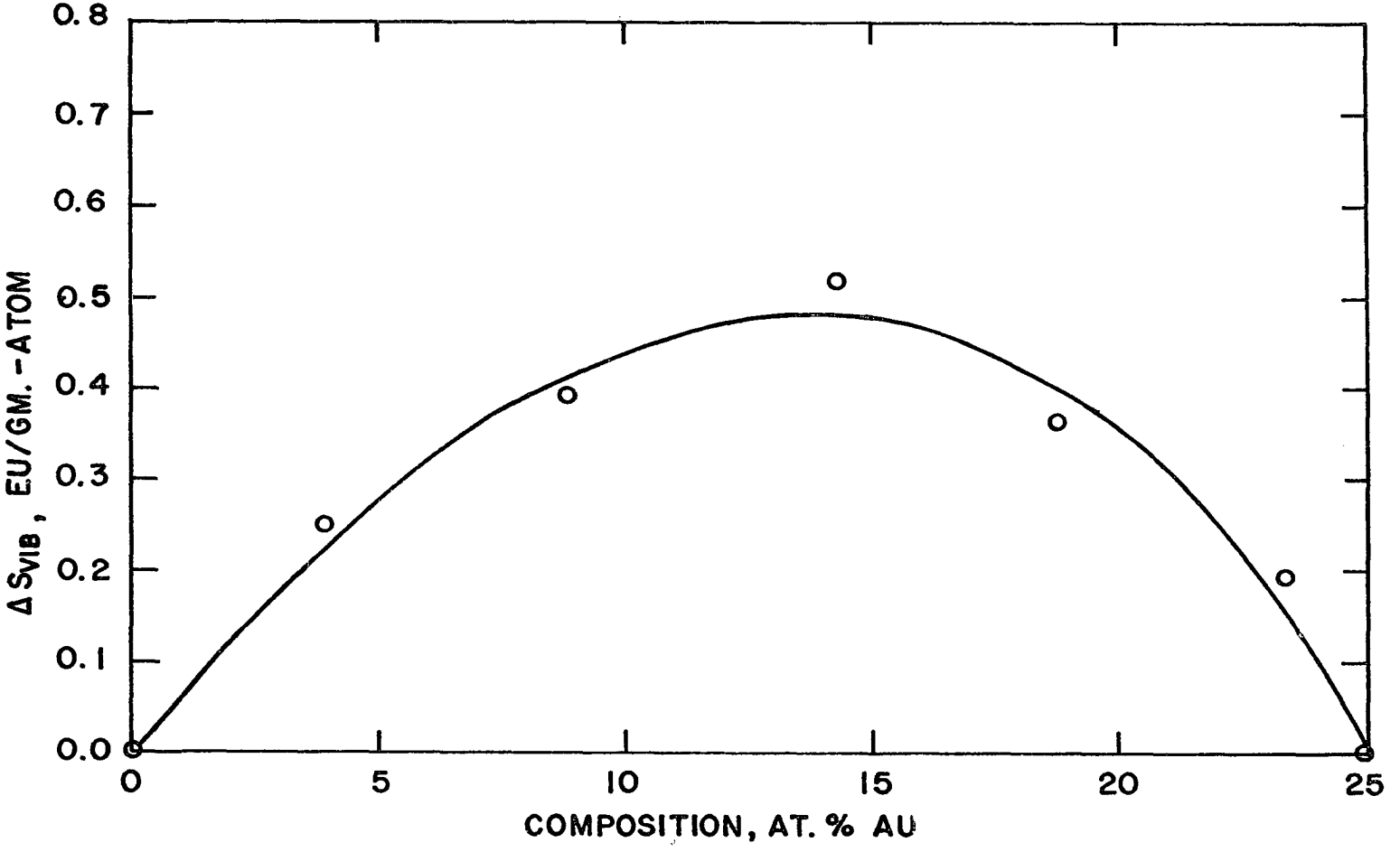


Figure 16. The calculated entropy of vibration at 300°K as a function of composition

form for dilute compositions and falls back to zero for the ordered stoichiometric composition. Then the sum of the excess configurational and vibrational entropies does indeed exhibit the required cusp at the ordered composition.

E. Analysis of Elastic Constants

In the following digression, I would like to show that neither the behavior of the "sea" of conduction electrons, or the overlap of the ion cores--the "usual" determinants of elastic behavior--can account for this decrease in the dilute range. By elimination, some other change in the electronic structure must be the cause, and I claim that changes in the Fermi energy and their contribution to the elastic moduli are the required sources. This claim thus infers that there are large changes in the electronic structure.

The original formulation of Fuchs' theory involved analysis and assessment of the various contributions to the energy of elastically strained crystals: an electronic term, W_E, and ion-core overlap (exchange) term, W_I, a Fermi energy term, W_F, the van der Waal's term, W_V, and the unstrained internal energy, W_0 (38). Double differentiation of these components with respect to two types of volume-conserving strains leads to expressions for the contributions to $C = C_{44}$ and $C' = (C_{11} - C_{12})/2$. For most of the investigations of noble metal alloys, it has been presumed that W_E and W_I account for nearly all of the strain dependent energy and various authors have attempted to fit their data to Fuchs' theory by the introduc-

tion of two parameters; α--descriptive of the ion-core overlap term and Z--an effective valence of the solute species when in solid solution (3, 34, 39-41).

However, when a lattice is elastically deformed in shear, the position of the Fermi level and the shape of the equi-energy surfaces change as the zone faces approach or recede from the center of the zone (42). Thus the density of states curve is intersected differently by the strained energy levels; the electrons redistribute themselves differently in reciprocal space, altering the Fermi energy with the degree and type of strain, and so produce a contribution to the elastic moduli. Since the density of states is highest near a zone boundary, the effect is maximized when the equi-energy contours pass near or contact a zone boundary, as is the case with pure copper (43), and inevitably, with dilute, copper-base alloys.

1. Fuchs' analysis

Fuchs' original model was applied to the pure noble metals with satisfactory results without consideration of the Fermi term. The basic assumptions are: 1. a metal is made up of atomic nuclei and the closed shells of electrons immersed in a uniform sea of valence electrons. 2. There is no deformation of the spherical ion-cores on approaching other ions in the lattice. This permits representation of this term by an exponential, for instance, of the Born-Mayer type used in the previous analysis. This premise should not go unquestioned,

for we now know that there is a certain "directionality" associated with the d-band electrons, which will undoubtedly produce deviations from sphericity of the ion-core. These nonspherical contours are probably not dependent on alloying elements or atomic volume changes. By and large, recent experimental and theoretical work justifies the use of a spherical potential for core-electron interactions. The reader is referred to a recent review by Watson and Ehrenreich (44) for a discussion of the electronic structure of the transition and noble metals and its relation to cohesive energy.

The extension of this method to alloys necessitates several additional assumptions. All valence electrons contributed by the solute must be distributed evenly in the sea of electrons. This seriously violates Friedel's theories of localized electron densities, but may become cogent at higher compositions where every third or fourth atom is an impurity specie. Since gold is probably no more polarizable than copper, this assumption should not apply to this isoelectronic alloy system. Most authors assume, as did I, that the ion-core interaction potential is simply a compositionally weighted average of the potential characterizing the pure species--again assuming that no deformation of the ion-cores exists.

The various contributions to the shear moduli, as detailed by Fuchs, and adapted to these measurements, are described below.

a. Electrostatic energy The C_E and C'_E have been derived to be:

$$C_E = 0.9479Z^2e^2/(1/2)a^4 \text{ dyne/cm}^2$$
$$C'_E = 0.1058Z^2e^2/(1/2)a^4 \text{ dyne/cm}^2 \qquad (20)$$

where Z = 1 for Cu-Au alloys. These terms slightly decrease on addition of gold to copper, as the lattice parameter increases. As shown below, the net effect of the electrostatic terms must be dominated by the ion-core repulsive and Fermi energy contributions.

b. Van der Waal's energy It is plausible that the relatively large radius of the d-shells of the noble metals may lead to polarization of the electrons in this level. This would give rise to a binding energy of the van der Waal's type. However, Friedel, who was largely responsible for this suggestion, later asserted that this did not seem to hold much promise (45), and later work (44) bears this out. On his authority, we may pretermit such a contribution.

c. Ion-core repulsion (exchange) energy As a consequence of the Pauli Exclusion Principle, a repulsion energy is developed when two ion-cores are positioned on nearby lattice sites. This energy is shear-dependent and the respective contributions derived by Fuchs for f.c.c. crystals are:

$$C_R = 1/2 \frac{4}{a_o^3}\left[r^2 \frac{d^2W_R}{dr^2} + 3r\frac{dW_R}{dr}\right] \text{ dyne/cm}^2$$

$$C_R' = 1/4 \frac{4}{a_o^3} \left[r^2 \frac{d^2 W_R}{dr^2} + 7r \frac{dW_R}{dr} \right] \text{ dyne/cm}^2 \qquad (21)$$

where W_R is a potential descriptive of the system under consideration. I have chosen to use a Born-Mayer potential of the form:

$$W_R(r) = A_R \exp (-\alpha_R(1 - r/r_R)) \qquad (22)$$

where A_R and α_R are characteristic of the pure metal (Cu or Au) and r_R is the interatomic distance in the pure species. The constants A_R and α_R have no particular physical significance, are usually derived from pressure studies (42, 46) and are listed in Table 9. The method used is analogous to

Table 9. Parameters used in the theoretical ion-core overlap contribution to the elastic shear moduli of Cu-Au alloys

Metal	r_o (10^{-8} ergs/cm)	A_R (10^{-13} ergs/cm)	α_R
Cu	2.556	0.768	13.68
Au	2.884	0.586	16.25

that used by Golding et al. (46), and needs no further description.

The analysis of this group of alloys divides naturally into that of dilute alloys and off-stoichiometric ordered alloys, or those to the left and right of the long-range order boundary which is at approximately 17 a/o Au.

1) Dilute alloys Using the above formulation, several variations of an f.c.c. solid solution model were used to calculate the ion-core contribution to the elastic moduli. The most basic is to assume that all atoms are centered on the lattice sites. The results of plotting $C_R'(x)/C_R'(0)$ are shown in Figure 17 as the curve labeled $\Upsilon = 1.0$. Scaling the Cu-Au interaction yields the curve for $\Upsilon = 0.9$.

For a more realistic calculation, we have allowed for a static displacement of the Cu species surrounding an Au atom. Several forms of this scalar, called Δr, were tested, roughly corresponding to values of static displacements recorded in the literature. This crude model should give some indication of the behavior of C_R and C_R' for very dilute alloys.

The results of these calculations, for three forms of Δr, are also shown in Figure 17. Even the static displacement models predict an initially positive slope for this term. As expected, there does not appear to be any reasonable model which will predict a decreasing ion-core contribution for the dilute alloys of Au in Cu. The Fermi energy term must dominate the behavior in this range.

2) Off-stoichiometric alloys A single calculation of C_R' for Cu_3Au yields the point shown in Figure 17. A similar value applies to C_R. We have assumed no static displacements, a fully ordered alloy, and $\Upsilon = 1.0$. It is interesting to note that the ratio of the measured elastic constants (1.11) is closely given by the ratio of $(C_R'(0.25) + C_E'(0.25))/$

Figure 17. The normalized ion-core overlap contribution to the elastic stiffness, C', of Cu-Au alloys, for various models, as a function of composition

1. constant r:

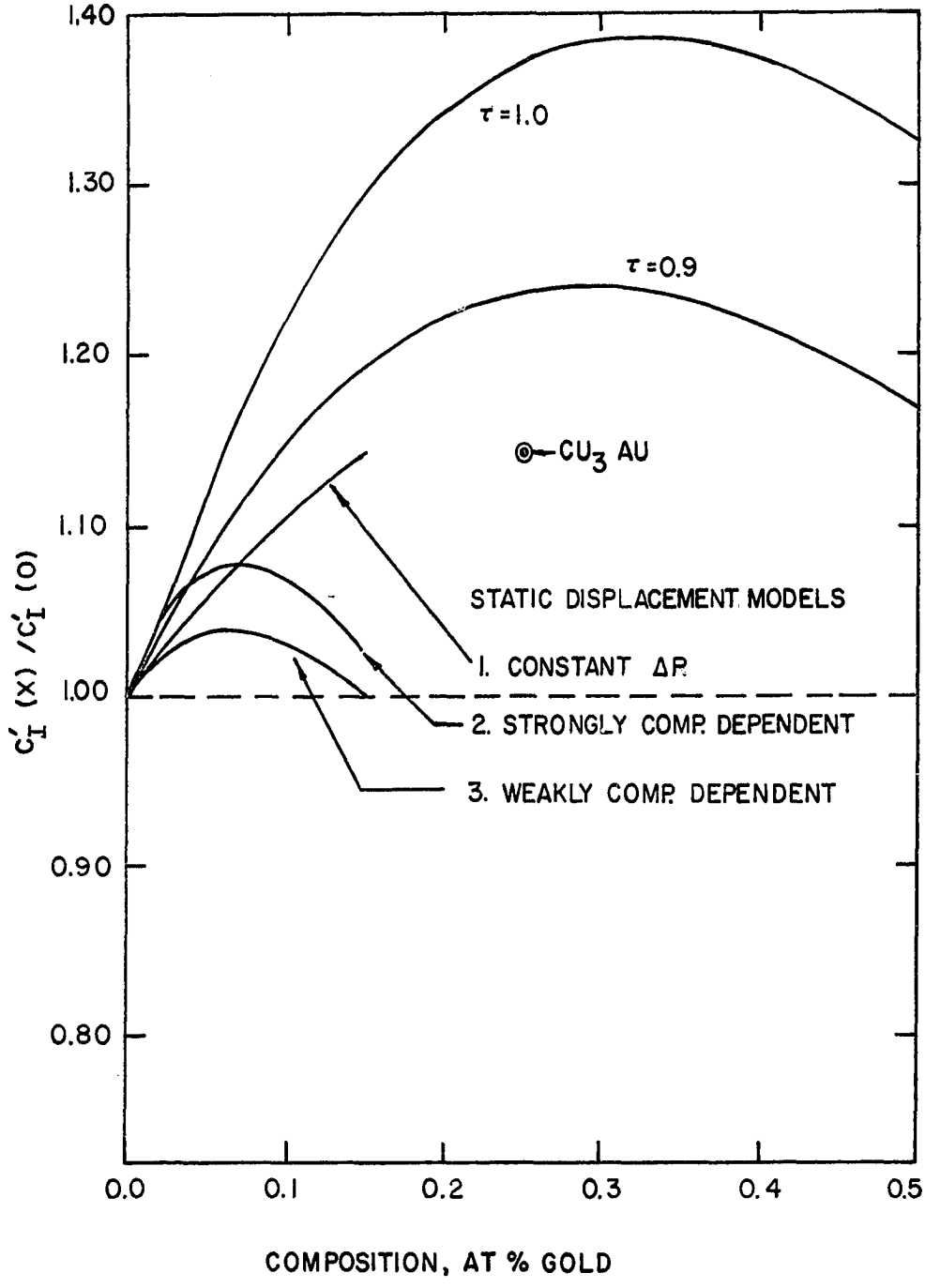
$$\Delta r = 0.5 \text{ Å}$$

2. strongly composition dependent r:

$$\Delta r = 0.75x \text{ Å}$$

3. weakly composition dependent r:

$$\Delta r = 0.05 + \frac{x}{2} \text{ Å}$$


1.40
1.30
1.20
1.10
1.00
0.90
0.80
$C_I'(X)/C_I'(0)$
$\tau = 1.0$
$\tau = 0.9$
$\circledcirc$—CU_3 AU
STATIC DISPLACEMENT MODELS
1. CONSTANT ΔP
2. STRONGLY COMP. DEPENDENT
3. WEAKLY COMP. DEPENDENT
0.0
0.1
0.2
0.3
0.4
0.5
COMPOSITION, AT % GOLD

$(C'_R(0) + C'_E(0)) = 1.14$

d. Fermi energy The work of Rayne (39) and Jones (47) on α and β brasses produced the first viable treatment of the Fermi energy contribution to the elastic constants of noble metal alloys. Their work is based on the fact that motion of the {111} zone boundaries under the respective shear strains generates a first-order effect on C_{44} but a (negligible) second-order effect on $C' = (C_{11} - C_{12})/2$. This predicts a negative C_F term, and a lower value of the calculated $C = C_{44}$ modulus, which is in qualitative agreement with the measured values. Flinn, McManus and Rayne (3) later extended this same conclusion to their analysis for the elastic constants of ordered and disordered Cu_3Au.

However, Collins (42) working with an 8-6 cone model, which provides a more accurate description of the density of states and the Fermi energy, suggests that although the C' shear does indeed cause a second-order motion of the {111} faces, the density of states will vary so rapidly near the zone boundary that the net contribution to C'_F may be appreciable, and so C' will also reflect Fermi surface effects.

If we assume that the ion-core contribution is substantially the same for C and C', then the isotropy ratio (Figure 12) gives some indication of the relative effect of the Fermi energy contribution to the elastic shear moduli.

In view of the fact that for dilute alloys, no reasonable description of the ion-core overlap term and the electrostatic

energy term predicts a C or C' which decrease as gold content increases, the Fermi energy contribution must certainly play a large role in determining the elastic stiffness of these alloys. Flinn et al. correctly predicted that C_F would be appreciable, but the scope of their efforts did not show that C_F' is also large, and both C_F and C_F' must decrease rapidly in the dilute region. Thus, it is my conclusion that this behavior and analysis is an indication of the changes in the electronic structure of these alloys as gold content increases.

As the ordered domains begin to form in the off-stoichiometric Cu_3Au alloys, the change in structure factor introduces new Brillouin zone boundaries in reciprocal space. These effect complicated changes in the density of states and intersect the Fermi surface in an entirely different way than in the dilute alloys. Of the two new influential zones, the $\{100\}$ set is completely contained within the Fermi surface, and has no effect. However, the $\{110\}$ faces intersect the surface, and calculations show that motion of this zone face has a first order effect on both C and C' shears. There is no clear resolution to this complicated problem, especially in view of Flinn's findings that ordering slightly decreases C_{44} but greatly increases $(C_{11} - C_{12})/2$.

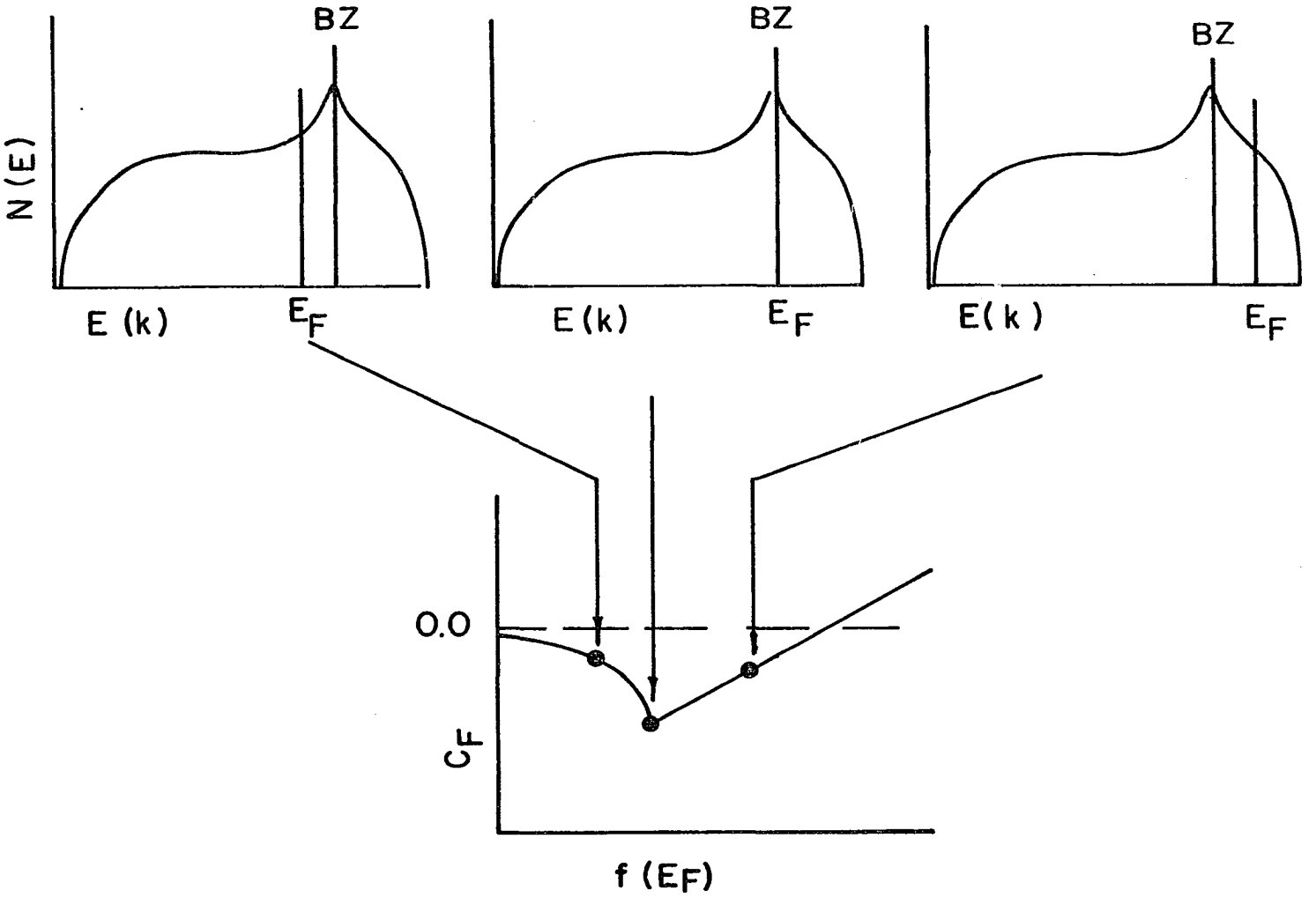
The exact calculation of the Fermi energy term must await precise measurement of the Fermi surface parameters. However, a qualitative explanation is possible on the basis of the proposed Fermi surface for the copper-rich, Cu-Au system (48).

It has been postulated that as Au is introduced to the Cu lattice, the Fermi surface tends to be more spherical, i.e., it approaches the free electron model. However, for any metal for which the Fermi surface contacts the Brillouin zone, it is the area of contact which controls the change in the shear constants--the less contact, the more negative the contribution (42). At the exact point of de-contact with the Brillouin zone, the shear constants have their most negative values. After de-contact occurs, the motion of the zone faces makes available to the electrons regions of the surface with an increasingly higher density of states. Electrons redistribute themselves, W_F decreases, and the C_F and C_F', while always negative, tend to zero as the distance from zone face to Fermi surface increases. (See series of drawings in Figure 18.)

A consideration of the motion of the faces in an f.c.c. reciprocal lattice shows that shifts of the $\{111\}$ faces have a first order effect on C and shifts of the $\{200\}$ faces have a first order effect on C'. Since the Fermi surface of pure Cu is well removed from the $\{200\}$ faces, but contacts the $\{111\}$ faces, we thus deduce that this contribution to C(= C_{44}) will be appreciable. In particular, C_F will be negative for Cu and become more negative as Au is added and the area of contact decreases.

The picture for C' is less clear. We would expect the controlling influence to be the motion of the $\{200\}$ zone faces. Since the Fermi surface is relatively well-removed from these,

Figure 18. The relative positions of the Brillouin zone face on the density of states distribution and the probable effect on the Fermi energy contribution to the elastic shear moduli


BZ
BZ
BZ
N(E)
E (k)
E_F
E(k)
E_F
E(k)
E_F
0.0
C_F
f (E_F)

the contribution is minimal. However, although the shear effects a second order change in the norm of the <111> zone vectors, the large change in the density of states would offset this. This would suggest that C_F' would also tend toward more negative values, but not as rapidly as C_F. Indeed, we find this to be the case. After accounting for the volume dependent correction (See Appendix) we find:

$$\left.\frac{dC'}{dx}\right|_{V,x=0} = -0.097 \times 10^{12} \text{ dynes/cm}^2\text{/mole fraction} \quad (23)$$

$$\left.\frac{dC}{dx}\right|_{V,x=0} = -0.34 \times 10^{12} \text{ dynes/cm}^2\text{/mole fraction} \quad (24)$$

We have thus seen that the Fermi energy contribution to the elastic moduli of dilute alloys may be the controlling factor. Definitive proof rides on a precise calculation of the ion-core and Fermi terms which is not possible at this time. However, if Collin's work with an 8-6 cone model is at all realistic, we know that the Fermi term has the magnitude necessary to dominate the ion-core terms.

2. Failure of Z-α analysis

The essence of these results questions the credibility of the previous analyses of the elastic stiffnesses of noble metal alloys. Confronted with the evidence that the Fermi energy contribution to the elastic moduli of copper-gold alloys is as large as it is, I wonder about the magnitude of this term for other noble metal alloys. On the other hand, the empirical Z,α parameters of various authors have produced

satisfactory explanations of the behavior of the moduli. Collins faced this fact with chagrin when his treatment did not produce the hoped for improvement in theoretical and empirical agreement of C and C'. This Z-α analysis is typically used when the behavior (i. e., shapes, curvatures) of the C_{exp} and C'_{exp} curves are about the same. The equations consider that the change in the elastic constants upon alloying are divided into two parts: that due to lattice expansion (or contraction), and the remainder due to alloying per se.

$$\Delta C_{exp} = C_{exp,\ solvent} - C_{exp,\ alloy}$$
$$= \Delta C_{lattice} + \Delta C_{alloying} \qquad (25)$$

If we now consider an alloy for which the lattice parameter is held constant, then we would expect the Z nonlocalized valence electrons would increase the electronic part, C_E or C'_E, by a factor Z^2, and if the bond energy W is proportional to the concentration x, we would have

$$C_{alloy,\ constant\ a_o} = Z^2\ C_{E,\ solvent} + (1 + \alpha x)\ C_{I,\ solvent} \qquad (26)$$

Subtracting

$$C_{solvent,\ a} = C_{E,\ solvent} + C_{I,\ solvent} \qquad (27)$$

we get

$$\Delta C_{alloying} = (Z^2 - 1)\ C_{E,\ solvent} + \alpha x C_{I,\ solvent} \qquad (28)$$

So

$$\Delta C_{exp} - \Delta C_{lattice} = (Z^2 - 1)\ C_{E,\ solvent}$$

$$+ \alpha \times C_{I,\ \text{solvent}} \qquad (29)$$

and a similar equation for C'.

However, the simplicity of these parameters disguises the fact that all the assumptions are absorbed in the "effective" valence Z, and the α term, which is in some way proportional to the "effective" ion-core radius. As pointed out by Smith, the C' equation essentially determines α, since $C'_I >> C'_E$ (See appendix). If, however, any other term affects the experimental value of C' of the solid solution, α will be accordingly in error.

The behavior of the elastic moduli measured in this work graphically demonstrates the misleading interpretations possible under these assumptions. For if one calculates the slope of $C_{exp}|_{x=0}$ and $C'_{exp}|_{x=0}$, corrects them for lattice expansion, and applies the Z-α analysis, he finds:

$$\alpha = -0.44$$
$$Z = 1.00 \qquad (30)$$

The implication of a negative α is that the Au ion-core is smaller than the Cu ion-core in the expanded lattice, a very unrealistic conclusion.

In the cases in which the behavior of C differs considerably from C', various authors have invoked some form of a Fermi energy term C_F; C'_F has been assumed to be negligible, since the C' deformation causes only a second order motion of the Brillouin zone faces. As I have pointed out, the evalua-

tion of these terms is extremely difficult, especially C_F', which is not negligible, at least in this case, and probably not in others.

Collins' work describes the dependence of the shape of the Fermi surface on e/a ratio, and as such, cannot be used to describe isoelectronic alloys such as Cu-Au. A model for CuAu alloys must depend on a postulate for the changing band structure with lattice parameter--information which is not yet available. Double differentiation of the Fermi energy with respect to the strains and evaluation for different U_{111} and U_{200} (42, equation 26) would then give more realistic values of C_F and C_F'.

Collins' effort was well-founded on a theoretical basis, but his attempts to find some experimental correlation in previous literature failed. He assumed that the ion-core interaction was not composition dependent, however, merely allowing for the expansion of the lattice as a correction to the data. His procedure is tantamount to assuming $\alpha = 0$ in the $Z-\alpha$ analysis. He further let Z = e/a, the electron per atom ratio, although this would seem to introduce a relatively minor error.

V. SUMMARY

That's how it is, said Pooh.

A. A. Milne - When We Were Six

This project craves another.

Shakespeare - Hamlet

My original thesis was that the electronic structure and vibrational spectra of copper-rich, Cu-Au alloys are strongly composition dependent. I purport to have demonstrated this through examination of the composition dependencies of the elastic moduli and the Debye temperatures calculated from the electrical resistivities and elastic moduli.

The evidence for the change in the electronic structure is based on the process of elimination. Neither the electrostatic term or the ion-core overlap term in the Fuchsian analysis of the elastic moduli can explain the behavior of the moduli in dilute Cu-Au alloys. The only other term of sufficient numeric magnitude is the Fermi energy term, which reflects changes in the position of the Fermi surface with respect to the Brillouin zone boundary. Analysis of the experimental evidence suggests that the area of contact of the Fermi surface on the $\{111\}$ Brillouin zone face is decreasing with increasing Au content.

The evidence for the change in the vibrational spectra

is based on analysis of the composition dependence of the Debye temperatures calculated from the values of the elastic moduli, and the temperature dependence of the electrical resistivity. In both cases, there is a rapid decrease in the values of the respective θ's as gold content increases. This decrease is far in excess of a linear extrapolation between the pure elements.

This investigation leaves many doors unopened. I have not been able to detail all the ramifications of the extreme slow-cooling of the alloys, although, from the lattice parameter measurements, some physical consolidation of the molar volume is obvious. Work at the University of Maryland (C. Gilmore, private communication, 1970-1971) indicates that the thermal displacements, i.e., the amplitude of the thermally-driven atomic vibrations, decrease in magnitude after longer heat treatments. The initial change between quenched alloys and those cooled over a thirty day period indicate about a 15% decrease. Analysis of the diffuse x-ray scattering would yield more information about the precise nature of this mechanism. Analysis of thermal neutron scattering would yield information on the phonon spectra, and would indicate whether the whole distribution is shifting with increasing gold content, or whether new modes are being created, or whether some other rearrangement of the phonon density is taking place.

There is a growing variety of experiments which indicate properties and parameters of the Fermi surface in alloys:

thermoelectric power, magnetoresistance, and lately, some measurements of the optical properties of metallic surfaces. While none of these are definitive, each provides more clues which may result in the indictment of one particular mechanism.

In short, while I have not been able to evaluate the parameters which detail the phonon distribution and the shape of the Fermi surface in Cu-Au alloys, I have tried to indicate the trends of these parameters, and the experimental consequences of their behavior.

More than anything else, I realize that this work is simultaneously a commendation and condemnation of the use of Debye theory. The parallel behavior of θ_R and θ_D is certainly a plus. On the other hand, much is left unexplained. This one-parameter theory is no substitute for a force-constant model, from which a more precise phonon distribution can be calculated. In addition, the precise Fermi surface morphology has not been revealed. I have only been able to add one clue to the slowly unraveling plot which indicates that the Fermi surface sphericizes somewhat as Au content increases.

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VII. APPENDIX

A. Numerical Calculation of Z, α Parameters

The numerical calculation of the Z, α parameters is not difficult, however, there are various ways to go about it. I am including this Appendix as an attempt to bring some unity to these procedures and contrast the possible variations.

The terms on the right of this equation

$$\Delta C_{\text{lattice}} = \Delta C_{E,\ \text{lattice}} + \Delta C_{I,\ \text{lattice}} \qquad (A1)$$

are found by differentiating Fuchs' expressions for C_E and C_I, equations 20 and 21 herein, with respect to a, the lattice parameter of the alloy, yielding these four expressions for f.c.c. metals:

$$\Delta C_{E,\ \text{lattice}} = -4\frac{\Delta a}{a} C_{E,\ \text{solvent}}$$

$$\Delta C'_{E,\ \text{lattice}} = -4\frac{\Delta a}{a} C'_{E,\ \text{solvent}}$$

$$\Delta C_{I,\ \text{lattice}} = +\frac{\Delta a}{a}\left(-\frac{r}{\rho} - 2 + \frac{r/\rho}{r/\rho - 3}\right) C_{I,\ \text{solvent}}$$

$$\Delta C'_{I,\ \text{lattice}} = +\frac{\Delta a}{a}\left(-\frac{r}{\rho} - 2 + \frac{r/\rho}{r/\rho - 7}\right) C'_{I,\ \text{solvent}} \qquad (A2)$$

where

$a = a_{o,\ \text{solvent}} - a_{o,\ \text{alloy}}$

r = nearest neighbor distance in f.c.c. alloy

ρ = interaction parameter

These values are then substituted into equations 28 or 29, herein, which are simultaneously solved for Z and α.

The difficulty with this method is that ρ is a quantum-

mechanical variable which is derived from a theoretical explanation of the pressure dependence of the bulk modulus. Fuchs has attempted a calculation of the components of C and C' for the noble and alkali metals, but we can put little confidence in the values.

To obviate this difficulty, we utilize the pressure dependence of the shear moduli themselves in a direct way, to give us the necessary lattice contribution to the moduli. If M stands for any elastic modulus, then the variation in M with composition is due to two effects: 1. the explicit change in M due to alloying and 2. the implicit change in M due to a change in the atomic volume, i.e., lattice parameter. Mathematically,

$$\frac{dM(x, a)}{dx} = \frac{\partial M}{\partial x}_a + \frac{\partial M}{\partial a}_x \frac{\partial a}{\partial x} \qquad (A3)$$

in words, the total empirical change in M equals the sum of the changes as a result of alloying plus the change as a result of lattice dilation. This is redefined in terms of measurable quantities in the following way. Differentiate the logarithm of the modulus,

$$\left.\frac{\partial \ln M}{\partial x}\right|_a = \frac{d \ln M}{dx} - \frac{1}{M} \frac{\partial M}{\partial P} \frac{\partial P}{\partial V} \frac{\partial V}{\partial a} \frac{\partial a}{\partial x}$$

$$\left.\frac{\partial \ln M}{\partial x}\right|_a = \frac{1}{M} \frac{dM}{dx} - \frac{1}{M} \frac{\partial M}{\partial P} \frac{3a^3}{a} \frac{\partial P}{\partial V} \frac{\partial a}{\partial x}$$

$$\left.\frac{\partial \ln M}{\partial x}\right|_a = \frac{1}{M} \frac{dM}{dx} - \frac{1}{M} \frac{\partial M}{\partial P} \frac{3V}{a} \frac{\partial P}{\partial V} \frac{\partial a}{\partial x}$$

finally arriving at

$$\frac{1}{M}\frac{\partial M}{\partial x}\Big|_a = \frac{1}{M}\frac{dM}{dx} + 3\,B_T\left(\frac{1}{M}\frac{\partial M}{\partial P}\right)\left(\frac{1}{a}\frac{\partial a}{\partial x}\right) \qquad (A4)$$

If one prefers,

$$\frac{1}{M}\frac{\partial M}{\partial x}\Big|_a = \frac{1}{M}\frac{dM}{dx} - \frac{1}{M}\frac{\partial M}{\partial P}\frac{\partial P}{\partial a}\frac{\partial a}{\partial x}$$

$$= \frac{1}{M}\frac{dM}{dx} - \left(\frac{1}{M}\frac{\partial M}{\partial a}\right) a \left(\frac{1}{a}\frac{\partial a}{\partial x}\right) \qquad (A5)$$

since it would be more accurate to measure the change in lattice parameter, or dilation synchronously with the change in modulus under pressure.

At any rate, the terms on the right of A4 or A5 are empirically available. Unfortunately, the determination of the pressure dependence of the elastic moduli is rather difficult and there are wide variations in the published values (49-51) which can considerably affect evaluation of $\frac{1}{M}\frac{\partial M}{\partial x}\Big|_a$, as shown below.

A model Z, $\propto$ evaluation procedure follows, using the pressure data of Salama and Alers (51), which was carefully experimentally determined, and is representative of all the pressure work done on pure copper. All the other parameters are obtained from this dissertation or unpublished research.

$$\frac{1}{C}\frac{\partial C}{\partial x}\Big|_a = \frac{1}{C}\frac{dC}{dx} + 3\,B_T\,\frac{1}{M}\frac{\partial M}{\partial P}\left(\frac{1}{a}\frac{\partial a}{\partial x}\right)$$

$$= -2.26 + 3\,(1.42)\left(\frac{1}{0.818}\right)(2.5)\,(0.148)$$

$$= -2.26 + 1.92 = -0.34 \qquad (A6)$$

Similarly

$$\frac{1}{C'}\frac{\partial C'}{\partial x}\Big|_a = \frac{1}{C'}\frac{dC'}{dx} + 3\,(1.42)\,\left(\frac{1}{0.256}\right)\,(0.45)\,(0.148)$$

$$= -1.48 + 1.10 = -0.38 \qquad \text{(A7)}$$

From these calculations, equations 23 and 24, herein, follow directly.

Although this method successfully avoids the introduction of any quantum-mechanical constants, we can no longer proceed with the Z-α analysis without using Fuchs' or somebody's theoretical values for the electronic and ion-core contributions to the elastic shear moduli. These are given below.

$$\frac{1}{a}\frac{da}{dx} = 0.148 \text{ / mole fraction}$$

$$C_E = 0.257 \times 10^{12} \text{ dynes/cm}^2$$

$$C_E' = 0.029 \times 10^{12} \text{ dynes/cm}^2$$

$$C_I = 0.64 \times 10^{12} \text{ dynes/cm}^2$$

$$C_I' = 0.22 \times 10^{12} \text{ dynes/cm}^2 \qquad \text{(A8)}$$

Using them, we have on substitution into equation 29, herein,

$$\Delta C = 0.257(Z^2 - 1) + 0.64\alpha x$$

$$\Delta C' = 0.029(Z^2 - 1) + 0.22\alpha x \qquad \text{(A9)}$$

Since we have assumed the bond energy is proportional to x (page 65, line 16, herein), we can use any small value of x we like. For x = 0.05 mole fraction,

$$-0.014 = 0.257\,(Z^2 - 1) + 0.028\alpha$$

$$-0.005 = 0.029\,(Z^2 - 1) + 0.011\alpha \qquad \text{(A10)}$$

from which follows

$$Z = 1.00$$

$$\alpha = -0.44$$

As mentioned before, the value used for the pressure derivatives is reflected in the values of Z, α which are calculated. This can be seen in Table A1. There I have compiled the pressure derivatives of the shear moduli and the results of the associated Z-α analysis. These results run the gamut of pressure work that I know of, and we see the variance in α which is possible. Phenomenologically, this makes sense; increased pressure brings about an enhanced interaction of the ion-cores, so variations in pressure measurements do cause proportionate variations in α.

Table A1. Results of Z-α analysis using pressure derivatives due to various investigators

Authors	$\frac{dC}{dP}$	$\left.\frac{\partial C}{\partial x}\right\|_a$ (10^{12} dynes/cm^2 mole fraction)	$\frac{dC'}{dP}$	$\left.\frac{\partial C'}{\partial x}\right\|_a$ (10^{12} dynes/cm^2 mole fraction)	Z (x = 0.05)	α
Hiki, Granato (50)	2.63	- 0.20	0.375	- 0.14	1.02	- 0.76
Salama, Alers (51)	2.5	- 0.28	0.45	- 0.10	1.00	- 0.44
Daniels, Smith (49)	2.35	- 0.36	0.58	- 0.015	0.95	+ 0.26